

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
25 November 2004 (25.11.2004)

PCT

(10) International Publication Number  
WO 2004/101137 A1

(51) International Patent Classification<sup>7</sup>: B01J 13/04,  
C04B 38/02

MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG,  
PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,  
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,  
ZW.

(21) International Application Number:  
PCT/AU2004/000241

(22) International Filing Date: 25 February 2004 (25.02.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/471,400 16 May 2003 (16.05.2003) US

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(81) Designated States (unless otherwise indicated, for every  
kind of national protection available): AE, AG, AL, AM,  
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,  
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,  
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,  
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,

(84) Designated States (unless otherwise indicated, for every  
kind of regional protection available): ARIPO (BW, GH,  
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), Euro-  
pean (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR,  
GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK,  
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,  
ML, MR, NE, SN, TD, TG).

#### Declarations under Rule 4.17:

— as to applicant's entitlement to apply for and be granted  
a patent (Rule 4.17(ii)) for the following designations AE,  
AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ,  
CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE,  
EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS,  
JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA,  
MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM,  
PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ,  
TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM,  
ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD,  
SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY,  
KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG,  
CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT,  
LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ,  
CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,  
TG)

— of inventorship (Rule 4.17(iv)) for US only

#### Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: METHODS FOR PRODUCING LOW DENSITY PRODUCTS

(57) Abstract: The method of preparing a low-density material and precursor for forming a low-density material. An aqueous mixture of inorganic primary component and a blowing agent is formed, the mixture is dried and optionally ground to form an expandable precursor. Such a precursor is then fired with activation of the blowing agent being controlled such that it is activated within a predetermined optimal temperature range. Control of the blowing agent can be accomplished via a variety of means including appropriate distribution throughout the precursor, addition of a control agent into the precursor, or modification of the firing conditions i.e. oxygen deficient or fuel rich environment, plasma heating etc.

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## **METHODS FOR PRODUCING LOW DENSITY PRODUCTS**

### **Technical Field**

The present invention relates to methods of forming low density products and  
5 particularly methods and formulations for synthetically preparing engineered expanded  
microparticles.

### **Background of the Invention**

Any discussion of the prior art throughout the specification should in no way be  
considered as an admission that such prior art is widely known or forms part of common  
10 general knowledge in the field.

Cenospheres are spherical inorganic hollow microparticles (microspheres) found  
in fly ash, which is produced as a by-product in coal-fired power stations. Cenospheres  
typically make up around 1-2% of the fly ash and "harvested" cenospheres are widely  
commercially available. The composition, form, size, shape and density of cenospheres  
15 provide particular benefits in the formulation and manufacture of many low-density  
products.

One of the characterizing features of cenospheres is their exceptionally high  
chemical durability. This exceptionally high chemical durability is understood to be due  
to the very low content of alkali metal oxides, particularly sodium oxide, in their  
20 composition. Accordingly, low-density composites produced from harvested  
cenospheres have the desirable properties of high strength to weight ratio and chemical  
inertness. Chemical inertness is especially important in Portland cement applications,  
where relative chemical inertness plays an important role in achieving highly durable  
cementitious products. Thus, harvested cenospheres have proven to be especially useful  
25 in building products and in general applications where they may come into contact with  
corrosive environments.

Despite the known utility of harvested cenospheres, their widespread use has  
been limited to a large extent by their cost and availability. The recovery of cenospheres  
in large quantities from fly ash is a labour intensive and expensive process. Although it  
30 is possible to increase the recovery of cenospheres from fly ash by modifying the  
collection process, the cost of improved recovery does not make this economically  
viable.

It may also be possible to alter combustion conditions in power stations to increase the yield of cenospheres in fly ash. However, combustion conditions in power stations are optimised for coal-burning rather than cenosphere production, and it is not economically viable to increase the yield of cenosphere production at the expense of coal-burning efficiency.

Several methods for producing microspheres are described in the prior art. An early method for manufacturing hollow glass microspheres involved combining sodium silicate and borax with a suitable foaming agent, drying and crushing the mixture, adjusting the size of the crushed particles and subsequently firing the particles. However, this method suffers from the use of expensive starting materials (e.g. borax). Hence, the resulting microspheres are necessarily expensive. In addition, the product has poor chemical durability due to a high percentage of sodium oxide in the resulting glass composition.

US 3,365,315 describes a method of producing glass microspheres from glass beads by heating in the presence of water vapour at a temperature of about 1200°C. This method requires the exclusive use of pre-formed amorphous glasses as the starting raw materials.

US 2,978,340 describes a method of forming glass microspheres from discrete, solid particles consisting essentially of an alkali metal silicate. The microspheres are formed by heating the alkali metal silicate at a temperature in the range of 1000-2500°F in the presence of a gasifying agent, such as urea or Na<sub>2</sub>CO<sub>3</sub>.

US Patent Application No. 2001/0043996 (equivalent of EP-A-1156021) describes a spray combustion process for forming hollow microspheres having a diameter of from 1 to 20 microns. However, this process is unsuitable for making hollow microspheres having a diameter similar to that of known cenospheres (i.e. about 200 microns). In spray combustion processes, rapid steam explosion ruptures larger particles, thereby preventing formation of hollow microspheres greater than about 20 microns in diameter.

US Patent Application No. 2002/0025436 describes a process for forming solid microspheres from fly ash. The process is said to improve the spheroidal uniformity of fly ash particles and provides fly ash spheroids having a density of about 1.8 g/cm<sup>3</sup>.

US 4,826,788 discloses a method of using two blowing agents activated at different temperatures to make large, foam glass granules greater than 1 mm in diameter.

However, the blowing agents discussed therein are limited to the blowing agents discussed therein are limited to one of the two agents must be an oxygen generating agent.

Generally speaking, prior art methods for forming engineered expanded  
5 microparticles involve firing an inorganic material in the presence of a blowing, gasifying or foaming agent.

Such blowing, gasifying or foaming agents should only be activated when the material from which the microparticle is produced, is in an appropriate form, ie liquid. However, it is sometimes extremely difficult to match the blowing agent with the  
10 material from which the microparticle will be formed and using the blowing agent in the most efficient manner.

It would be desirable to have a system which allowed a greater degree of control over the process.

It is an object of the present invention to overcome or ameliorate at least one of  
15 the disadvantages of the prior art, or to provide a useful alternative.

#### Summary of the Invention

In a first aspect, the present invention provides a method of producing a low density material comprising:

providing a precursor by forming an aqueous mixture of an inorganic primary  
20 component and a blowing component, drying the mixture and optionally grinding a predetermined particle size and firing the precursor to activate the blowing component to expand the precursor and form a low density material wherein

activation of the blowing agent is controlled such that the blowing agent is activated within a predetermined optimal temperature range.

25 In a preferred embodiment, control of the blowing agent is accomplished by providing a control agent in the precursor which conserves and/or protects the blowing agent until the mixture reaches the aforementioned optimal temperature range.

The control agent can be provided in a number of forms. In one form, the control agents comprise materials which react under certain process conditions to alter the  
30 environment of the precursor and thereby control activation of the blowing agent. For instance, control agents can be in the form of additional blowing agents. To explain, the precursor formulation can include a primary blowing agent which acts primarily to expand the precursor material and form the expanded microparticles. Control agents in

the form of secondary and tertiary blowing agents may be included in the precursor mixture. These blowing agents can be activated at lower temperatures than the primary blowing agent. Many blowing agents are activated by oxidation. Activating tertiary and/or secondary blowing agents results in scavenging of oxygen from the process environment thereby controlling activation of the primary blowing agent. As will be clear to a person skilled in the art, this allows conservation and release of the primary blowing agent within the preferred optimal temperature range providing better control and more efficient use of the blowing agent in the process.

Control of the blowing agent can be accomplished by a variety of means. For instance the process could be run within an oxygen deficient environment thereby reducing exposure of the blowing components to oxygen. When the precursor mixture reaches the optimal temperature range, oxygen could be introduced to the process to thereby activate the blowing agent.

Another alternative is to run the firing process in a fuel rich fashion, ie less oxidising. Other firing mechanisms such as plasma heating etc could be used with appropriate dosing of  $O_2$  depleting or  $O_2$  enriching gases to control activation of the blowing agent.

In still a further embodiment, conservation of the blowing agent can be accomplished physically. Distribution of the blowing agent throughout the precursor particles can be such that at least some of the blowing component is maintained within the core of the precursor away from the surface. When such a precursor particle is subjected to heat, the surface temperature will rise and the core temperature will lag behind the surface temperature. This temperature differential will be engineered such that the blowing agent is activated only when substantially the entire precursor particle reaches the optimal temperature range.

In this regard, the optimal temperature range is one in which the precursor mixture reaches the optimal viscosity for the expansion process. The optimal temperature range will depend upon a number of parameters including the make up on the inorganic primary component, the make up of the blowing agents and control agents, precursor particle size, desired density of resultant low density material.

Preferably, the low density material is produced in the form of microparticles, most preferably with a particle size of up to 1,000 microns.

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In a second aspect the present invention provides a method of forming a precursor for a low density material comprising the steps of:

- (a) providing an inorganic primary component;
- (b) forming an aqueous mixture of the inorganic primary component, a blowing agent and a control agent, and;
- (c) drying the mixture to provide an expandable precursor for forming a low density material wherein

said blowing agent and control agent are selected to control activation of the blowing agent such that the blowing agent is activated within a predetermined optimal temperature range.

In a third aspect the present invention provides a method of forming a precursor for a low density material comprising the steps of:

- (d) providing an inorganic primary component;
- (e) forming an aqueous mixture of the inorganic primary component and a blowing agent; and
- (f) drying the mixture to provide an expandable precursor for forming a low density material wherein

said blowing agent is selected and/or distributed in the precursor to control activation of the blowing agent upon firing of the precursor such that the blowing agent is activated within a predetermined optimal temperature range.

In a fourth aspect the present invention provides a precursor suitable for producing expanded micro particles, said precursor comprising an expandable inorganic primary component, a blowing agent adapted to be activated and thereby expand said primary component, and a control agent selected to control activation of the blowing agent such that the blowing agent is activated within a predetermined optimal temperature range.

In a fifth aspect the present invention provides a precursor suitable for producing expanded micro particles, said precursor comprising an expandable inorganic primary component and a blowing agent selected and/or distributed within the precursor to control activation of the blowing agent whereby upon firing of the precursor to produce the expanded micro particles, the blowing agent is activated within a predetermined optimal temperature range.

In a sixth aspect the present invention provides a method of controlling activation of the blowing agent in an inorganic mixture to produce expanded micro particles, said method comprising:

- 5 providing at least one blowing agent which is activated under predetermined conditions to release a blowing gas and produce expanded micro particles and controlling such conditions whereby said activation takes place within a predetermined optimal viscosity range of the inorganic mixture.

- 10 In a seventh aspect the present provides a blowing component for producing expanded micro particles, said blowing component comprising a primary blowing agent and a predetermined quantity of compatible control agent wherein upon inclusion of such a blowing component within an expandable mixture, the control agent may be activated prior or simultaneously with the blowing agent to control and conserve the blowing agent.

- 15 In a preferred embodiment, the control agent is activated at a lower temperature than the blowing agent. The control agent may act to alter the process environment and render it less conducive to activation of the blowing agent. For instance, the control agent may act to alter the oxygen content for scavenge oxygen from the process environment and thereby render such an environment less conducive to an oxidation activatable blowing agent.

- 20 In another preferred form, the blowing component/agent comprises a series of blowing compounds adapted to be sequentially activated over a range of process conditions.

- In another embodiment, the present invention provides a method of controlling activation of a blowing agent in an inorganic mixture to produce expanded  
25 microparticles, said method comprising:

providing at least one blowing agent which is activated under predetermined conditions to release a blowing gas and produce expanded microparticles and controlling conditions such that said activation takes place within a predetermined optimal viscosity range of the inorganic mixture.

- 30 The inorganic mixture melts at relatively high temperatures. It is important that the blowing agent only be activated when the inorganic mixture is at its optimal viscosity, since, as will be clear to persons skilled in the art, this will provide the greatest yield from the expansion process. Accordingly, the present invention provides a

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mechanism for tailoring the blowing agent such that it is activated at the optimal viscosity of the inorganic mixture, ie within a particular temperature range.

Unless the context clearly requires otherwise, throughout the description and the claims, the words 'comprise', 'comprising', and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

As used herein, the term "engineered/expanded microparticle" means a hollow microparticle synthesized as a primary target product of a synthetic process. The term does not include, for example, harvested cenospheres which are merely a by-product of burning coal in coal-fired power stations.

Although the terms "microsphere" and "microparticle" are used throughout the specification, it will be appreciated that these terms are intended to include any substantially rounded discrete microparticle, including those that are not true geometric spheres.

As used herein, the term "precursor" refers to the agglomerate or particle made from the suitable formulation prior to its expansion to form one or more expanded microparticles. The term "control agent" refers to a components included in the precursor which controls activation of the blowing component.

As used herein, the term "primary component" means that this component is usually the major constituent of the formulation/precursor, in the sense that the amount of primary component usually exceeds the amounts of the other constituents. Moreover, the term "inorganic primary component" means that the primary component consists essentially of inorganic materials. However, small amounts (e.g. up to about 10 wt.%) of other materials may still be included in the inorganic primary component.

As used herein the term "activation" refers to the conditions, eg temperature, redox of the oxides present in the formulation, and gaseous atmosphere during thermal treatment ( e.g. oxygen partial pressure) range at which a blowing component is activated and releases its blowing gas.

The preferred method of the present invention advantageously provides a means for producing expanded microparticles in excellent yield from widely available and inexpensive starting materials. Hence, the method, in its preferred form, reduces the overall cost of producing microparticles, and consequently increases the scope for their use, especially in the building industry, and all filler applications such as in polymeric



composites where the use of presently available cenospheres is relatively limited due to their prohibitive cost and low availability. The present invention recognises the critical importance of controlling activation of the blowing agent(s) in achieving reliable synthesis of expanded microparticles from a wide range of materials.

5 Preferred features of all aspects of the present invention are described in more detail below.

Method of Forming Precursor to the Expanded Microparticle

The precursor for producing the expanded microparticle can be produced by combining the primary component, blowing component and optionally, control agent in  
10 an aqueous mixture. This aqueous mixture is then dried to produce an agglomerated precursor.

As described above, the present invention provides a method of forming a precursor, which includes the steps of mixing and drying. The resultant precursor is generally a substantially solid agglomerate mixture of its constituent materials.

15 Typically, the mixing step provides an aqueous dispersion or paste, which is later dried. Mixing can be performed by any conventional means used to blend ceramic powders. Examples of preferred mixing techniques include, but are not limited to, agitated tanks, ball mills, single and twin screw mixers, and attrition mills.

Certain mixing aids (e.g. surfactants) may be added in the mixing step, as  
20 appropriate. Surfactants, for example, may be used to assist with mixing, suspending and dispersing the particles.

Drying is typically performed at a temperature in the range of 30 to 600°C and may occur over a period of up to about 48 hours, depending on the drying technique employed. Any type of dryer customarily used in industry to dry slurries and pastes may  
25 be used in the present invention.

Drying may be performed in a batch process using, for example, a stationary dish or container. Alternatively, drying may be performed in a spray dryer, fluid bed dryer, rotary dryer, rotating tray dryer or flash dryer.

Preferably, the mixture is dried such that the water content of the resultant  
30 agglomerate precursor is less than about 14 wt.%, more preferably less than about 10 wt.%, more preferably less than about 5 wt.%, and more preferably about 3 wt.% or less. It was found that with 14 wt.% water or more in the precursor, it tends to burst into fines

upon firing. It is understood by the present inventors that this bursting is caused by rapid steam explosion in the presence of too much water.

Hence, the resultant precursor should preferably be essentially dry, although a small amount of residual moisture may be present after the solution-based process for its formation. Indeed, a small amount of water may help to bind particles in the precursor together, especially in cases where particles in the precursor are water-reactive.

Preferably, the dried precursor particles have an average particle size in the range of 10 to 1000 microns, more preferably 30 to 1000 microns, more preferably 40 to 500 microns, and more preferably 50 to 300 microns. The particle size of the precursor will be related to the particle size of the resultant synthetic hollow microsphere, although the degree of correspondence will, of course, only be approximate. If necessary, standard comminuting/sizing/classification techniques may be employed to achieve this preferred average particle size.

Drying is most preferably performed using a spray dryer having an aqueous feed. It has been found that spray drying has several advantages when used in the present invention.

Method of Forming Precursor Using a Spray Dryer

As discussed above, the present invention envisages various techniques for controlling activation of the blowing agent such that it is activated at the optimum point in the production process. Such control can be achieved by combining a control agent in the precursor formulation. Another embodiment includes a series of control agents and/or blowing agents such that there is sufficient blowing/expanding gas available at the optimal temperature. In one embodiment, a series of blowing agents may be used which are sequentially activated as temperature rises.

Yet a further embodiment involves distributing the blowing agent throughout the precursor such that while the precursor is being fired, the blowing agent distributed near the surface is exposed to a high temperature but the blowing agent near the core of the precursor is "physically" protected. To explain, the thermal conductivity of the formulation causes a delay between application of heat on the surface of the precursor to temperature rise within the core of the precursor. Accordingly, blowing agent which is within the core of the precursor will not be activated until a major portion of the precursor particle has already reached its optimal temperature.

Still further, as discussed above, many blowing agents are activated by oxidation. Particles within the core of the precursor will not be exposed to oxygen to the same extent as blowing agent on the surface, further protecting the blowing agent in the core of the particle.

- 5        Rather surprisingly, the Applicant has found that spray dryers are not only useful for forming precursors to the expanded microparticles but are also excellent at providing the aforementioned optimal distribution of the blowing agent within the precursor. Not wishing to be bound by any particular theory, it would appear that blowing agents which are water soluble tend to come to the surface during the spray dry production technique.
- 10       Non water soluble blowing agents tend to remain within the core. Accordingly, one can design a mixture of blowing agents which provide initial, subsequent and final activation according to their water solubility. An example may be sugar which is useful as a blowing agent but is water soluble. During the spray dry technique, this blowing agent will tend to migrate to the surface of the precursor. Silicone carbide on the other hand,
- 15       which is also a useful blowing agent is non water soluble and does not migrate to the surface of the precursor.

Spray dryers are described in a number of standard textbooks (e.g. *Industrial Drying Equipment*, C.M. van't Land; *Handbook of Industrial Drying 2<sup>nd</sup> Edition*, Arun S. Mujumbar) and will be well known to the skilled person.

- 20       In addition to the aforementioned advantages, it is generally desirable to synthesize expanded microparticles having a predetermined average particle size and a predetermined (preferably narrow) particle size distribution. The use of a spray dryer in the present invention has been found to reduce the need for any sizing/classification of the precursors or, ultimately, the synthetic expanded microparticles. Spray drying has the
- 25       additional advantage of allowing a high throughput of material and fast drying times. Hence, in a particularly preferred embodiment of the present invention, the drying step is performed using a spray dryer.

It has been determined that the particle size and particle size distribution can be affected by one or more of the following parameters in the spray drying process:

- 30       -        inlet slurry pressure and velocity (particle size tends to decrease with increasing pressure);
- design of the atomizer (rotary atomizer, pressure nozzle, two fluid nozzle or the like)

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- design of the gas inlet nozzle;
- volume flow rate and flow pattern of gas; and
- slurry viscosity and effective slurry surface tension.

Preferably, the aqueous slurry feeding the spray dryer comprises 25 to 75% w/v solids, more preferably 40 to 60% w/v solids.

In addition to the ingredients described above, the aqueous slurry may contain further processing aids or additives to improve mixing, flowability or droplet formation in the spray dryer. Suitable additives are well known in the spray drying art. Examples of such additives are sulphonates, glycol ethers, cellulose ethers and the like. These may be contained in the aqueous slurry in an amount ranging from 0 to 5 % w/v.

In the spray drying process, the aqueous slurry is typically pumped to an atomizer at a predetermined pressure and temperature to form slurry droplets. The atomizer may be one or a combination of the following: an atomizer based on a rotary atomizer (centrifugal atomization), a pressure nozzle (hydraulic atomization), or a two-fluid pressure nozzle wherein the slurry is mixed with another fluid (pneumatic atomization).

In order to ensure that the droplets formed are of a proper size, the atomizer may also be subjected to cyclic mechanical or sonic pulses. The atomization may be performed from the top or from the bottom of the dryer chamber. The hot drying gas may be injected into the dryer co-current or counter-current to the direction of the spraying.

It has been found that by controlling the spray drying conditions, the average particle size of the precursors and the precursor particle size distribution can be controlled. For example, a rotary atomizer has been found to produce a more uniform agglomerate particle size distribution than a pressure nozzle. Furthermore, rotating disc atomizers allow higher feed rates, suitable for abrasive materials, with negligible blockage or clogging. In some embodiments, a hybrid of known atomizing techniques may be used in order to achieve agglomerate precursors having the desired characteristics.

The atomized droplets of slurry are dried in the spray dryer for a predetermined residence time. The residence time can affect the average particle size, the particle size distribution and the moisture content of the resultant precursors. The residence time is preferably controlled to give the preferred characteristics of the precursor, as described

above. The residence time can be controlled by the water content of the slurry, the slurry droplet size (total surface area), the drying gas inlet temperature and gas flow pattern within the spray dryer, and the particle flow path within the spray dryer. Preferably, the residence time in the spray dryer is in the range of 0.1 to 10 seconds, although relatively long residence times of greater than 2 seconds are generally more preferred.

Preferably, the inlet temperature in the spray dryer is in the range of 300 to 600°C and the outlet temperature is in the range of 90 to 220°C.

Spray drying advantageously produces precursors having this narrow particle size distribution. Consequently, synthetic expanded microparticles resulting from these precursors will have a similarly narrow particle size distribution and consistent properties for subsequent use.

A further surprising advantage of using a spray dryer is that the resultant precursors have an improved intra-particle distribution of constituents. While the atomized droplets are resident in the spray dryer, water is rapidly pulled from the interior to the exterior, thus forming a concentration gradient of soluble species in the agglomerate, with relatively water-soluble species being more concentrated towards the exterior. Another advantage of spray drying is to form dried cellulated agglomerated precursors according to the method of present invention (e.g. pre-foaming). The entrained gas will further expand during the foaming process to lower the density of the product which otherwise may not have been possible to achieve with multi blowing agents. By this optional and yet novel method, low temperature gas forming compounds are added to the precursor before the drying process. The gas forming compound can be activated either by physical means such as degassing due to a reduction in surface tension (reverse temperature solubility), or by chemical means. An example of chemical gasification at low temperature is decomposition of carbonates to CO<sub>2</sub> by changing the pH, or use of appropriate organic compounds such as air entraining agents customarily used in concrete.

For an efficient and reliable synthesis of hollow microspheres, the precursor should ideally have a high concentration of glass-forming material at the surface, which can form a molten glassy skin during firing. Furthermore, the precursor should ideally have a concentration of blowing agent near the core, which can release a blowing gas for entrapment within the glassy skin during firing. With careful selection of materials, this ideal intra-particle distribution can be achieved using the spray drying method.

Inorganic Primary Component

Preferably, the amount of inorganic primary component comprises at least 40 wt.% based on the total dry weight of the agglomerate precursor, more preferably at least 50 wt.%, more preferably at least 60 wt.%, more preferably at least 70 wt.% and more  
5 preferably at least 80 wt.%.

The preferred ratio of primary component to other components, eg blowing agent will vary, depending on the composition of each of these ingredients. Typically, the ratio of primary component to blowing agent will be in the range of 1000:1 to 10:1, more preferably, 700:1 to 15:1, and more preferably 500:1 to 20:1.

10 Preferably, the inorganic primary component comprises at least one material selected from inorganic oxides, non-oxides, salts or combinations thereof. Such materials may be industrial and/or residential by-products, minerals, rocks, clays, technical grade chemicals or combinations thereof. One of the advantages of the present invention is that it allows the synthesis of hollow microspheres from inexpensive  
15 industrial and/or residential waste products. Accordingly, the inorganic primary component may comprise materials such as fly ash, bottom ash, blast-furnace slag, paper ash, waste glasses (e.g. soda lime glasses, borosilicate glasses or other waste glasses), waste ceramics, kiln dust, waste fibre cement, concrete, incineration ash, diatomaceous earth, silica sand, silica fume, or combinations thereof.

20 Preferably, the inorganic primary component is capable of forming a viscoelastic liquid when heated to a predetermined temperature. This viscoelastic liquid is preferably a glass-forming liquid.

Preferably, the inorganic primary component comprises at least one compound in an oxide form, which can form a majority of a glass phase. Non-oxide components may  
25 oxidize and become part of the glass phase, except for those elements that can remain dissolved but not oxidized, such as halides.

In one preferred embodiment, the inorganic primary component comprises at least one silicate material. Silicate materials are well known to the person skilled in the art. Generally, these are materials having a relatively large component of silica ( $\text{SiO}_2$ )  
30 (i.e. greater than about 30 wt.%, preferably greater than 50% and more preferably greater than 60%). In most cases alumina is also a major oxide constituents of the silicate materials. The term of silicate in the present invention, hence covers all the aluminosilicate materials suitable as primarily compounds.

The amounts of silica and alumina in the silicate material will vary depending on the source and may even vary within the same source. Fly ash, for example, will contain varying amounts of silica and alumina depending on the type of coal used and combustion conditions. Preferably, the mass ratio of silica ( $\text{SiO}_2$ ) to alumina ( $\text{Al}_2\text{O}_3$ ) is greater than about 1. Typically, silicate materials for use in this preferred embodiment of the present invention have a composition of 30 to 95 wt.%  $\text{SiO}_2$ ; 0 to 45 wt.% (preferably 2 to 45 wt.%)  $\text{Al}_2\text{O}_3$ ; up to about 30 wt.% (preferably up to about 15 wt.%) divalent metal oxides (e.g.  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SrO}$ ,  $\text{BaO}$ ); up to about 50 wt.% monovalent metal oxides (e.g.  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ); and up to about 20 wt.% of other metal oxides, including metal oxides which exist in multiple oxidation states (e.g.  $\text{SnO}_2$ ,  $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$  etc.).

Typical silicates, which may be used in this embodiment of the present invention are fly ash (e.g. Type F fly ash, Type C fly ash etc.), waste glass, bottom ash, blast-furnace slag, paper ash, basaltic rock, andesitic rock, feldspars, silicate clays (e.g. kaolinite clay, illite clay, bedalite clay, bentonite clay, china, fire clays etc.), bauxite, obsidian, volcanic ash, volcanic rocks, volcanic glasses, geopolymers or combinations thereof.

Silicates, such as those described above, may form the majority of the inorganic primary component. For example, silicates may form at least 50 wt.%, at least 70 wt.%, or at least 90 wt.% of the inorganic primary component, based on the total weight of the inorganic primary component.

Fly ash, waste soda lime glass, andesitic rock, basaltic rock and/or clays are preferred source materials for the inorganic primary component. Fly ash is a particularly preferred inorganic primary component due to its low cost and wide availability. In one form of the invention, the primary component comprises at least 5 wt.% fly ash, and more preferably at least 10 wt.% fly ash, based on the total amount of primary component. In another form of the invention, the inorganic primary component comprises at least 50 wt.% fly ash, at least 70 wt.% fly ash, or at least 90 wt.% fly ash, based on the total amount of inorganic primary component. In some embodiments of the present invention, the inorganic primary component may include a geopolymer, which is formed when a silicate is contacted with an aqueous solution of a metal hydroxide (e.g.  $\text{NaOH}$  or  $\text{KOH}$ ). Geopolymers are well known in the art.

The inorganic primary component may be either calcined or non-calcined. The term "calcined" means that the inorganic material has been heated in air to a predetermined calcination temperature for a predetermined duration so as to either oxidise or pre-react certain component(s). Calcination of the inorganic material may be advantageous in the present invention since the blowing (expansion) process can be sensitive to the redox state of multivalent oxide(s) present in the inorganic material. Without wishing to be bound by theory, it is believed that activation of the blowing agents is influenced by the release of oxygen from multivalent oxide(s) present in the inorganic material (e.g. by redox reaction). As an example, a carbonaceous blowing agent may react with oxygen released from ferric oxide ( $\text{Fe}_2\text{O}_3$ ) to form  $\text{CO}_x$  (where x can be 1 or 2 depending on carbon oxidation state) which is in turn reduced to ferrous oxide ( $\text{FeO}$ ). The release of  $\text{CO}_x$  from the blowing agent expands the microsphere. Hence, by pre-calcinating the inorganic material in air, the relative amount of ferric oxide is increased, which is then used as a source of oxygen for blowing agents to produce more gas, thereby lowering the density of the microparticles.

In addition, calcination can promote pre-reaction of oxide components and/or cause partial vitrification in the inorganic material, which may be beneficial in the production of high quality microparticles.

In cases where high chemical durability is required, the primary inorganic component is preferably a low alkali material. By "low alkali material", it is meant a material having an alkali metal oxide content of less than about 10 wt.%. In this form of the present invention, relatively high alkali materials may still be included in the inorganic primary component. Accordingly, waste glass powders, such as soda lime glasses (sometimes referred to as cullet) having an alkali content of up to about 15 wt.% may be included.

Preferably, the inorganic primary component has an average primary particle size in the range of 0.01 to 100 microns, more preferably 0.05 to 50 microns, more preferably 0.1 to 25 microns, and more preferably 0.2 to 10 microns. Preferred particle sizes may be achieved by appropriate grinding and classification. All types of grinding, milling, and overall size reduction techniques that are used in ceramic industry can be used in the present invention. Without limiting to other methods of size reduction used for brittle solids, preferred methods according to the present invention are ball milling (wet and dry), high energy centrifugal milling, jet milling, and attrition milling. If more than one



inorganic material is to be used, then the multitude of ingredients can be co-ground together. In one method of the present invention, all the constituent materials of the agglomerate precursor are co-ground together before mixing (*e.g.* in a wet ball mill).

Blowing Component

5       The blowing agents used in the present invention are compounds which, when heated, liberate a blowing gas by one or more of combustion, evaporation, sublimation, thermal decomposition, gasification or diffusion. The blowing gas may be, for example, CO<sub>2</sub>, CO, O<sub>2</sub>, N<sub>2</sub>, N<sub>2</sub>O, NO, NO<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub>, H<sub>2</sub>O or mixtures thereof. Preferably, the blowing gas comprises CO<sub>2</sub> and/or CO.

10       Preferably, the amount of blowing component is in the range of 0.05 to 10 wt.% based on the total dry weight of the precursor, more preferably 0.1 to 6 wt.%, and more preferably 0.2 to 4 wt.%. The exact amount of blowing component will depend on the composition of the inorganic primary component, the types of blowing agents and the required density of the final hollow microsphere.

15       In one embodiment, the blowing component comprises a primary blowing agent and a secondary blowing agent. The primary blowing agent has a first activation temperature and the second blowing agent has a second activation temperature lower than the first activation temperature. In other words, in use, the secondary blowing agent is initially activated as temperature rises followed by the primary blowing agent.

20       This conserves the primary blowing agent.

Preferably, the primary blowing agent is selected from powdered coal, carbon black, activated carbon, graphite, carbonaceous polymeric organics, oils, carbohydrates such as sugar, corn syrup, starch; PVA, various amines, carbonates, carbides (*e.g.* silicon carbide, aluminium carbide), sulfates, sulfides, nitrides (aluminium nitride, silicon  
25       nitride, boron nitride), nitrates, polyols, glycols, glycerine or combinations thereof. Silicon carbide and carbon black are particularly preferred primary blowing agents.

Preferably, the secondary blowing agent is selected from, carbon, carbonaceous polymeric organics, oils, carbohydrates such as sugar, corn syrup, starch; PVA, various amines, carbonates, sulfates, sulfides, nitrides, nitrates, polyols, glycols, glycerine or  
30       combinations thereof. Carbon black, sugar, corn syrup and starch are particularly preferred secondary blowing agents.

In alternative embodiments of the present invention, the blowing component comprises further blowing agents, in addition to the primary and secondary blowing

agents described above. These additional blowing agents are designated tertiary, quaternary *etc.* blowing agents having corresponding third, fourth *etc.* activation temperatures.

Accordingly, in one alternative embodiment the blowing component further  
5 comprises a tertiary blowing agent having a third activation temperature, wherein the third activation temperature is less than the first activation temperature. Preferably, the third activation temperature is also less than the second activation temperature. The tertiary blowing agent may be selected from carbonaceous polymeric organics, oils, carbohydrates such as sugar, corn syrup, starch; PVA, various amines, sulfates, sulfides,  
10 nitrides, nitrates, polyols, glycols, glycerine or combinations thereof. Sugar, corn syrup, and starch are particularly preferred tertiary blowing agents.

Preferably, and particularly if the blowing agent is non-water soluble, the blowing agent has an average particle size of about 10 microns.

The use of multiple blowing agents has been shown to have particular benefits in  
15 the synthesis of expanded microparticles. It provides control of the blowing (expansion) process, thereby allowing a reliable synthesis of expanded microparticles from a wide range of readily available and inexpensive inorganic materials. Furthermore, it maximises the efficiency of high quality (and relatively expensive) primary blowing agents, which further reduces the cost of synthetically manufacturing expanded  
20 microparticles.

Without wishing to be bound by theory, it is believed that the primary blowing agent produces the majority of gas during the blowing (expansion) process when the precursor. The secondary (and, optionally, tertiary, quaternary *etc.*) blowing agent acts as a sacrificial material by reducing or preventing premature spending of the primary  
25 blowing agent, for example by vaporisation and/or oxidation, before the precursor material has become molten enough to capture the blowing gas during the expansion process.

For instance, a preferred blowing agent composition includes silicon carbide as a primary blowing agent and carbon or powdered coal as a secondary blowing agent.  
30 Carbon acts as the sacrificial blowing agent and starts to oxidize first keeping oxygen away from carbide until the precursor melts. Once the precursor melts, the majority of CO and CO<sub>2</sub> gas produced by oxidation of carbide is trapped within the molten precursor.

An alternative blowing agent composition comprises silicon carbide as the primary blowing agent, carbon as the secondary blowing agent, and sugar as the tertiary blowing agent. Without wishing to be bound by theory, it is believed that sugar starts to oxidize first preventing oxidation of carbon and carbide, then carbon begins to oxidize preventing oxidation of carbide, and then finally carbide oxidizes to CO and CO<sub>2</sub>, which are primarily responsible for blowing (expansion) of the microparticle. One advantage of the present method of invention is to reduce the overall cost of the blowing agent. Sugar is less costly than carbon, and silicon carbide is by far much more expensive than either one. By using the multi blowing agents, the amount of expensive silicon carbide required to produce a given low density product is dramatically reduced. Figure 2 depicts the TGA (thermal gravimetric analysis) of sugar, carbon, and silicon carbide in air. The activation temperatures with ascending order start with sugar, then carbon, and finally silicon carbide.

This novel mixture of blowing agents allows the use of inexpensive sacrificial blowing agents (e.g. sugar, carbon and/or powdered coal), in order to maximise the efficiency and blowing capacity of a more expensive primary blowing agent (e.g. silicon carbide).

As discussed earlier, an additional and important advantage is realised when the precursors are prepared using the spray drying method. By making use of the mechanism described above, whereby relatively water-soluble species are pulled towards the exterior of the precursor during spray drying, an advantageous intra-particle distribution of primary and secondary blowing agents can be achieved.

Hence, using a relatively water-insoluble primary blowing agent and a relatively water-soluble secondary blowing agent, the secondary blowing agent can migrate towards the surface of the precursor, leaving the primary blowing agent uniformly dispersed. With the primary and secondary blowing agents separated in this way, the secondary blowing agent can more effectively "scavenge" oxygen away from the primary blowing agent in the critical period during firing in which a glassy skin has not yet formed around the precursor. This scavenging effect protects the primary blowing agents against premature spending, thereby maximising its blowing capacity after (or during) formation of the glassy skin.

Sugar is an example of a useful secondary blowing agent. Sugar is soluble in water and will migrate towards the exterior of the precursor during spray drying. At the

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- same time, sugar can be converted to carbon at the spray drying temperature, resulting in a fine dispersion of carbon particles throughout the exterior part of the precursor. This fine dispersion of carbon particles acts as an effective secondary (sacrificial) blowing agent by scavenging oxygen away from a primary blowing agent (e.g. silicon carbide) during the initial period of firing.

Furthermore, organic compounds, such as sugar and starch, help to bind the agglomerate precursor constituents together. Thus, materials such as sugar and starch can act as both binding agents and blowing agents in the present invention.

#### Control Agent

- The secondary and tertiary blowing agents mentioned above act as control agents to protect and conserve the primary blowing agent in the precursor formulation. Persons skilled in the art will be aware of other materials which can be included in the precursor formulation and which can act to control activation of the blowing agent by, for example, scavenging oxygen in the process environment.

#### Binding Agent

- In a preferred embodiment of the present invention, a binding agent/agents (or binder) may be mixed with the inorganic primary component and blowing component. The primary function of the binding agent is to intimately bind the silicate particles in the precursor together. The binder also may be selected to react with the silicate materials to lower the viscosity of the resulting glassy microparticles at the firing temperature.

In general, any chemical substance that is reactive and/or adheres with the inorganic primary component can be used as the binding agent. The binder may be any commercially available material used as a binder in the ceramic industry.

- Preferably, the binding agent is selected from alkali metal silicates (e.g. sodium silicate), alkali metal aluminosilicates, alkali metal borates (e.g. sodium tetraborate), alkali or alkaline earth metal carbonates, alkali or alkaline earth metal nitrates, alkali or alkaline earth metal nitrites, boric acid, alkali or alkaline earth metal sulfates, alkali or alkaline earth metal phosphates, alkali or alkaline earth metal hydroxides (e.g. NaOH, KOH or Ca(OH)<sub>2</sub>), carbohydrates (e.g. sugar, starch etc.), colloidal silica, inorganic silicate cements, Portland cement, lime-based cement, phosphate-based cement, organic polymers (e.g. polyacrylates) or combinations thereof. In some cases, fly ash, such as ultrafine, Type C or Type F fly ash, can also act as a binding agent.

The binding agent and blowing agent are typically different from each other, although in some cases (e.g. sugar, starch etc.) the same substance may have dual blowing/binding agent properties, as described above.

The term "binder" or "binding agent", as used herein, includes all binding agents mentioned above, as well as the *in situ* reaction products of these binding agents with other components in the agglomerate. For example, an alkali metal hydroxide (e.g. NaOH) will react *in situ* with at least part of an inorganic primary component comprising a silicate to produce an alkali metal silicate. Sodium hydroxide may also form sodium carbonate when exposed to ambient air containing CO<sub>2</sub>, the rate of this process increasing at higher temperatures (e.g. 400°C). The resulting sodium carbonate can react with silicates to form sodium silicate.

Preferably, the amount of binding agent is in the range of 0.1 to 50 wt.% based on the total dry weight of the agglomerate precursor, more preferably 0.5 to 40 wt.% and more preferably 1 to 30 wt.%.

It has already been discussed above that it is preferred to have the binding agent towards the exterior of the precursor so that, during firing, the binding agent forms a molten skin. Formation of this molten skin should preferably be prior to or during activation of the blowing component, especially activation of the primary blowing agent. Not only will this formation of a molten skin further protect blowing agent within the precursor, it advantageously provides synthetic expanded microparticles of low density.

Using the spray drying method for forming the agglomerate precursor, it has been unexpectedly found that the concentration of the binding agent (as well as the blowing agents) within different zones of the agglomerate precursor can be controlled by appropriate selection of the solubility limits of this component. Accordingly, it is preferred that, using the spray drying method, the binding agent has a relatively high water-solubility so that it is more concentrated at the exterior of the agglomerate precursor and, hence, can form a molten skin during subsequent firing. Alkali compounds such as alkali hydroxides, or in particular compounds of sodium silicate and sodium aluminosilicate are preferred binding agents in this regard, since they are soluble in water and can, therefore, migrate towards the exterior of the agglomerate precursor.

#### Method of Forming Synthetic Expanded Microparticles

The precursors produced by the method described above may be used to synthesize expanded microparticles by firing at a predetermined temperature profile.

Preferably, the temperature profile during firing fuses the precursor into a melt, reduces the viscosity of the melt, seals the surface of the precursor and promotes expansive formation of gas within the melt to form bubbles. The temperature profile should also preferably maintain the melt at a temperature and time sufficient to allow gas bubbles to coalesce and form a single primary void. After foaming, the newly expanded particles are rapidly cooled, thus forming hollow glassy microsparticles. Accordingly, the temperature profile is preferably provided by a furnace having one or more temperature zones, such as a drop tube furnace, a vortex type furnace, a fluidised bed furnace or a fuel-fired furnace, with upward or downward draft air streams. A fuel-fired furnace includes furnace types in which precursors are introduced directly into one or a multitude of combustion zones, to cause expansion or blowing of the particles. This is a preferred type of furnace, since the particles benefit by direct rapid heating to high temperatures, which is desirable. The heat source may be electric or provided by burning fossil fuels, such as natural gas or fuel oil. However, the preferred method of heating is by combustion of natural gas, since this is more economical than electric heating and cleaner than burning fuel oil.

Typically, the peak firing temperature in firing step (b) is in the range of 600 to 2500°C, more preferably 800 to 2000°C, more preferably 1000 to 1500°C, and more preferably 1100 to 1400°C. However, it will be appreciated that the requisite temperature profile will depend on the type of inorganic primary component and blowing component used.

Preferably, the exposure time to the peak firing temperature described above will be for a period of 0.05 to 20 seconds, more preferably 0.1 to 10 seconds.

#### Synthetic Hollow Microspheres

The present invention further provides a synthetic hollow microsphere obtained by the method described above. Such hollow microparticle are inexpensive to produce and may be used advantageously as a cheap alternative to harvested cenospheres. Synthetic hollow microparticle according to the present invention typically comprise a substantially spherical wall with a closed shell (void) structure. The synthetic hollow microparticle preferably have one or more of the following characteristics, which are also generally characteristics of harvested cenospheres:

- (i) an aspect ratio of between about 0.8 and 1.

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(ii) a void volume of between about 30 and 95%, based on the total volume of the microsphere;

(iii) a wall thickness of between about 5 and 30% of the microsphere radius;

(iv) a composition of 30 to 85 wt.%  $\text{SiO}_2$ , 2 to 45 wt.% (preferably 6 to 40 wt.%)  $\text{Al}_2\text{O}_3$ , up to about 30 wt.% divalent metal oxides (e.g.  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SrO}$ ,  $\text{BaO}$ ), 2 to 10 wt.% monovalent metal oxides (e.g.  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ), and up to about 20 wt.% of other metal oxides, including metal oxides which exist in multiple oxidation states (e.g.  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$  etc.);

(v) a silica to alumina ratio which is greater than about 1;

(vi) an average diameter of between 30 and 1000 microns, more preferably between 40 and 500 microns. (An average diameter of 30 microns or above is advantageous, because such particles are not considered to be respirable dusts);

(vii) an outer wall thickness of between 1 and 100 microns, preferably between 1 and 70 microns, more preferably between 2.5 and 20 microns;

(viii) a particle density of between 0.1 and 2.0  $\text{g/cm}^3$ , more preferably between 0.2 and 1.5  $\text{g/cm}^3$ , and more preferably between 0.4 and 1.0  $\text{g/cm}^3$ ; or

(ix) a bulk density of less than about 1.4  $\text{g/cm}^3$ , preferably less than about 1.0  $\text{g/cm}^3$ .

#### Use of Synthetic Expanded Microparticles

The synthetic expanded microparticles according to the present invention may be used in a wide variety of applications, for example, in filler applications, modifier applications, containment applications or substrate applications. The scope of applications is much greater than that of harvested cenospheres due to the low cost and consistent properties of synthetic microspheres.

Synthetic microparticles according to the present invention may be used as fillers in composite materials, where they impart properties of cost reduction, weight reduction, improved processing, performance enhancement, improved machinability and/or improved workability. More specifically, the synthetic microparticles may be used as fillers in polymers (including thermoset, thermoplastic, and inorganic geopolymers), inorganic cementitious materials (including material comprising Portland cement, lime cement, alumina-based cements, plaster, phosphate-based cements, magnesia-based cements and other hydraulically settable binders), concrete systems (including precise concrete structures, tilt up concrete panels, columns, suspended concrete structures etc.),

putties (e.g. for void filling and patching applications), wood composites (including particleboards, fibreboards, wood/polymer composites and other composite wood structures), clays, and ceramics. One particularly preferred use is in fibre cement building products.

- 5       The synthetic expanded microparticles may also be used as modifiers in combination with other materials. By appropriate selection of size and geometry, the microparticles may be combined with certain materials to provide unique characteristics, such as increased film thickness, improved distribution, improved flowability *etc.* Typical modifier applications include light reflecting applications (e.g. highway markers and signs), industrial explosives, blast energy absorbing structures (e.g. for absorbing the  
10       energy of bombs and explosives), paints and powder coating applications, grinding and blasting applications, earth drilling applications (e.g. cements for oil well drilling), adhesive formulations and acoustic or thermal insulating applications.

- The synthetic expanded microparticles may also be used to contain and/or store  
15       other materials. Typical containment applications include medical and medicinal applications (e.g. microcontainers for drugs), micro-containment for radioactive or toxic materials, and micro-containment for gases and liquids.

- The synthetic expanded microparticles may also be used in to provide specific surface activities in various applications where surface reactions are used (*i.e.* substrate  
20       applications). Surface activities may be further improved by subjecting the microparticles to secondary treatments, such as metal or ceramic coating, acid leaching *etc.* Typical substrate applications include ion exchange applications (for removing contaminants from a fluid), catalytic applications (in which the surface of the microparticle is treated to serve as a catalyst in synthetic, conversion or decomposition  
25       reactions), filtration (where contaminants are removed from gas or liquid streams), conductive fillers or RF shielding fillers for polymer composites, and medical imaging.

#### Brief Description of the Drawings

      The present invention will now be described, by way of example only, with reference to the following drawings in which:

- 30       Figure 1 is a phase equilibrium diagram for binary system  $\text{Na}_2\text{O-SiO}_2$ , the composition being expressed as a weight percentage of  $\text{SiO}_2$ ;



Figure 2 is a TGA plot of three preferred blowing agents, sugar, carbon black and silicon carbide, showing sequential activation temperatures of sugar to be the lowest and carbide being the highest;

Figures 3 to 8 are scanning electron micrographs of synthetic hollow  
5 microspheres obtained from Example 1;

Figures 9 to 14 are scanning electron micrographs of synthetic hollow  
microspheres obtained from Example 2;

Figures 15 to 17 are scanning electron micrographs of synthetic hollow  
microspheres obtained from Example 3; and

10 Figures 18 to 19 are scanning electron micrographs of synthetic hollow  
microspheres obtained from Example 4;

Figure 20 is a scanning electron micrographs of synthetic hollow microspheres  
obtained from Example 5.

## 15 Detailed Description of Preferred Embodiments

### EXAMPLE 1

This example illustrates a method to make expanded micro-inclusions from formulations consisting of basalt and sodium hydroxide.

The formulations were prepared by mixing ground basalt with solid sodium  
20 hydroxide and water. Various mixtures of blowing agents with control agents including  
silicon carbide, sugar, carbon black and coal were added either in combination or  
isolation. The formulations are shown in Table 1. The composition of the basalt is given  
in Table 2.

#### Formulation 1A

25 This formulation illustrates a method to make expanded micro-inclusions from a  
formulation consisting of basalt, sodium hydroxide and sugar as the blowing agent.

A sample was prepared by mixing 92 grams of basalt; ground to a  $d_{50}$  particle  
size of about 2 microns, with 5 grams of solid sodium hydroxide (flakes), 3 grams of  
commercial sugar and 23mL of water. The formulation is shown in Table 1.

#### 30 Formulation 1B

This formulation illustrates a method to make expanded micro-inclusions from a  
formulation consisting of basalt, sodium hydroxide and carbon black as the blowing  
agent.

A sample was prepared by mixing 94 grams of basalt; ground to a  $d_{50}$  particle size of about 2 microns, with 5 grams of solid sodium hydroxide (flakes), 1 gram of a commercial grade carbon black and 38mL of water. The formulation is shown in Table 1.

5 Formulation 1C

This formulation illustrates a method to make expanded micro-inclusions from a formulation consisting of basalt, sodium hydroxide and silicon carbide as the blowing agent.

10 A sample was prepared by mixing 94.5 grams of basalt; ground to a  $d_{50}$  particle size of about 1 micron, with 5 grams of solid sodium hydroxide (flakes), 0.5 grams of a commercial grade silicon carbide and 38mL of water. The formulation is shown in Table 1.

Formulation 1D

15 This formulation illustrates a method to make expanded micro-inclusions from a formulation consisting of basalt, sodium hydroxide, silicon carbide as the primary blowing agent and coal as the control agent or secondary blowing agent.

A sample was prepared by mixing 93.5 grams of basalt, 0.5 grams of a commercial grade silicon carbide and 1 gram of a commercial grade coal; the resulting blend being co-ground to a  $d_{50}$  particle size of about 1 micron. This blend was then  
20 mixed with 5 grams of solid sodium hydroxide (flakes) and 38mL of water. The formulation is shown in Table 1.

Formulation 1E

This formulation illustrates a method to make expanded micro-inclusions from a formulation consisting of basalt, sodium hydroxide, silicon carbide as the primary  
25 blowing agent and sugar as the control agent or secondary blowing agent.

A sample was prepared by mixing 92 grams of basalt; ground to a  $d_{50}$  particle size of about 1 micron, with 5 grams of solid sodium hydroxide (flakes), 0.5 grams of a commercial grade silicon carbide, 2.5 grams of a commercial sugar and 37mL of water. The formulation is shown in Table 1.

30 Formulation 1F

This formulation illustrates a method to make expanded micro-inclusions from a formulation consisting of basalt, sodium hydroxide, carbon black as the primary blowing agent and sugar as the control agent or secondary blowing agent.

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A sample was prepared by mixing 91.4 grams of basalt; ground to a  $d_{50}$  particle size of about 2 microns, with 4.8 grams of solid sodium hydroxide (flakes), 0.8 grams of a commercial grade carbon black, 3 grams of a commercial sugar and 38mL of water. The formulation is shown in Table 1.

5 Each mixture was blended into homogeneous slurry, poured into a flat dish and allowed to solidify at room temperature for approximately 5 minutes. The resulting product was further dried at about 50 degrees Celsius for about 20 hours, after which it was ground and sieved to obtain powders within a size range of 106 to 180 microns. In the next step, the powders were fed into a vertical heated tube furnace at an approximate  
10 feed rate of 0.14 g/min. The constant temperature zone of the furnace could be adjusted to provide residence times from less than one second to approximately several seconds at the peak firing temperatures. The foamed micro-inclusions were collected on a funnel shaped collecting device covered with a fine mesh screen positioned at the bottom portion of the furnace. A mild suction was applied to the end of funnel to aid in  
15 collecting the micro-inclusions. The products were characterized for particle density (e.g. apparent density), and microscopic examination by SEM. The results are summarized in Table 3.

Figures 3 to 9 show SEM examinations of the products obtained from formulations 1A to 1F respectively.

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Table 1. Formulations (grams) 1A to 1F

Formulation No.	Basalt	Sodium Hydroxide	Blowing Agent	Control Agent	Water (mL)
1A	92.0	5.0	3.0 Sugar	-	23
1B	94.0	5.0	1.0 Carbon Black	-	38
1C	94.5	5.0	0.5 SiC	-	38
1D	93.5	5.0	0.5 SiC	1.0 powdered coal	38
1E	92.0	5.0	0.5 SiC	2.5 Sugar	37
1F	91.4	4.8	0.8 Carbon Black	3.0 Sugar	38

Table 2. Composition of Basalt

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	Mn <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Total
46.1	15.8	11.4	9.5	9.6	0.0	2.8	1.5	2.4	0.25	0.59	99.94

5

Table 3. Result Summary

Formulation No.	Temperature (degree C)	Residence time (second)	Apparent density (g/cm <sup>3</sup> )
1A	1300	0.6-1.1	1.28
1B	1300	0.6-1.1	1.13
1C	1250	0.6-1.1	1.13
1D	1300	0.6-1.1	0.82
1E	1300	0.6-1.1	0.85
1F	1300	0.6-1.1	1.21

Following conclusions can be drawn from Example 1.

- 1- SiC is a more effective primary blowing agent than carbon and sugar to lower the particle density. Note that the net carbon content of SiC (30 wt% carbon) is less than equivalent mass of carbon in carbon (100 wt %), and sugar (40 wt% carbon).
- 2- Use of SiC with one or more control agents is more effective in lowering the particle density compared to any single blowing agent used in this example.
- 3- The combination of any single blowing agent with a control agent can be optimized to strongly influence the product's particle density, i.e. all SiC combinations are more effective to lower the particle density as compared to carbon-sugar combination.

**EXAMPLE 2**

This example illustrates a method to make expanded micro-inclusions from a formulation consisting of various silicate compounds, sodium hydroxide and multi-blowing agents.

- 5 Expanded micro-inclusions were prepared using blends of a soda lime waste glass and various silicate materials. These blends also include mixtures of a primary blowing agent with control agents of silicon carbide with control agents, sugar, and/or carbon black. The formulations are shown in Table 4. The composition of the waste glass used in this work is given in Table 5.

10 Formulation 2A

This formulation illustrates a method to make expanded micro-inclusions from a formulation consisting of glass, sodium hydroxide, with silicon carbide as the blowing agent and carbon black as the control agent.

- 15 A sample was prepared by mixing 95.6 grams of glass; ground to a  $d_{50}$  particle size of about 1 micron, with 3 grams of solid sodium hydroxide (flakes), 0.4 grams of a commercial grade silicon carbide, 1 gram of a commercial grade carbon black and 58mL of water. The formulation is shown in Table 4.

Formulation 2B

- 20 This formulation illustrates a method to make expanded micro-inclusions from a formulation consisting of glass, fly ash, sodium hydroxide, with silicon carbide as the blowing agent and carbon black as the control agent.

- A sample was prepared by mixing 65.5 grams of glass and 28.1 grams of fly ash; the mixture being co-ground to a  $d_{50}$  particle size of about 2 microns. The glass/fly ash blend was mixed with 5 grams of solid sodium hydroxide (flakes), 0.4 grams of a  
25 commercial grade silicon carbide, 1 gram of a commercial grade carbon black and 42mL of water. The formulation is shown in Table 4. The composition of the fly ash is given in Table 5.

Formulation 2C

- 30 This formulation illustrates a method to make expanded micro-inclusions from a formulation consisting of glass, basalt, sodium hydroxide, with silicon carbide as the blowing agent and carbon black as the control agent.

A sample was prepared by mixing 46.8 grams of glass and 46.8 grams of basalt; the mixture being co-ground to a  $d_{50}$  particle size of about 2 microns. The glass/basalt

blend was mixed with 5 grams of solid sodium hydroxide (flakes), 0.4 grams of a commercial grade silicon carbide, 1 gram of a commercial grade carbon black and 37mL of water. The formulation is shown in Table 4. The composition of the basalt is given in Table 5.

5 Formulation 2D

This formulation illustrates a method to make expanded micro-inclusions from a formulation consisting of glass, volcanic ash, sodium hydroxide, with silicon carbide as the blowing agent and carbon black as the control agent.

A sample was prepared by mixing 46.8 grams of glass and 46.8 grams of  
10 volcanic ash; the mixture being co-ground to a  $d_{50}$  particle size of about 2 microns. The glass/volcanic ash blend was mixed with 5 grams of solid sodium hydroxide (flakes), 0.4 grams of a commercial grade silicon carbide, 1 gram of a commercial grade carbon black and 50mL of water. The formulation is shown in Table 4. The composition of the volcanic ash is given in Table 5.

15 Formulation 2E

This formulation illustrates a method to make expanded micro-inclusions from a formulation consisting of glass, andesite, sodium hydroxide, with silicon carbide as the primary blowing agent and sugar as the control agent.

A sample was prepared by mixing 47.1 grams of glass and 47.1 grams of  
20 andesite; the mixture being co-ground to a  $d_{50}$  particle size of about 2 microns. The glass/andesite blend was mixed with 3 grams of solid sodium hydroxide (flakes), 0.4 grams of a commercial grade silicon carbide, 2.5 grams of sugar and 50mL of water. The formulation is shown in Table 4. The composition of the andesite is given in Table 5.

Formulation 2F

25 This formulation illustrates a method to make expanded micro-inclusions from a formulation consisting of glass, andesite, sodium hydroxide, with silicon carbide as the blowing agent and carbon black as the control agent.

A sample was prepared by mixing 47.8 grams of glass and 47.8 grams of andesite; the mixture being co-ground to a  $d_{50}$  particle size of about 1 micron. The  
30 glass/andesite blend was mixed with 3 grams of solid sodium hydroxide (flakes), 0.4 grams of a commercial grade silicon carbide, 1 gram of a commercial grade carbon black and 43mL of water. The formulation is shown in Table 4.

Each mixture was blended into homogeneous slurry, poured into a flat dish and allowed to solidify at room temperature for approximately 5 minutes. The resulting product was further dried at about 50 degrees Celsius for about 20 hours, after which it was ground and sieved to obtain powders within a size range of 106 to 180 microns. In the next step, the powders were fed into a vertical heated tube furnace at an approximate feed rate of 0.14 g/min. The constant temperature zone of the furnace could be adjusted to provide residence times from less than one second to approximately several seconds at the peak firing temperatures. The foamed micro-inclusions were collected on a funnel shaped collecting device covered with a fine mesh screen positioned at the bottom portion of the furnace. A mild suction was applied to the end of funnel to aid in collecting the micro-inclusions. The products were characterized for particle density (e.g. apparent density), and microscopic examination by SEM.

The results are summarized in Table 6.

Figures 10 to 16 show SEM cross sectional views for each of samples 2A to 2F.

Table 4. Formulations (grams) 2A to 2F

Formulation No.	Waste Glass	Additional Component	Sodium Hydroxide	Blowing Agent	Control Agent	Water (mL)
2A	95.6	-	3.0	0.4 SiC	1.0 Carbon Black	58
2B	65.5	28.1 fly ash	5.0	0.4 SiC	1.0 Carbon Black	42
2C	46.8	46.8 basalt	5.0	0.4 SiC	1.0 Carbon Black	37
2D	46.8	46.8 volcanic ash	5.0	0.4 SiC	1.0 Carbon Black	50
2E	47.1	47.1 andesite	3.0	0.4 SiC	2.5 Sugar	42
2F	47.8	47.8 andesite	3.0	0.4 SiC	1.0 Carbon Black	43

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Table 5. Chemical Compositions

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	Mn <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Total
Glass	74.7	2.0	0.9	11.1	0.6	0.0	10.0	0.5	0.06	0.06	0.02	99.94
Fly Ash	52.7	20.2	13.2	7.6	2.5	0.4	0.4	1.3	1.3	0.16	0.08	99.84
Volcanic Ash	76.4	12.4	2.1	0.9	0.3	0.0	2.1	5.5	0.15	0.08	0.03	99.96
Andesite	67.8	15.2	4.6	2.1	0.6	0.0	2.7	4.9	0.7	0.9	0.28	99.78

Table 6. Result Summary

Formulation No.	Temperature (degree C)	Residence time (second)	Apparent density (g/cm <sup>3</sup> )
2A	1200	0.6-1.1	0.98
2B	1300	0.6-1.1	1.11
2C	1200	0.6-1.1	0.93
2D	1200	0.6-1.1	0.94
2E	1300	0.6-1.1	0.93
2F	1300	0.6-1.1	0.77

5 The following conclusions can be drawn from Example 2.

- 1- The combination of blowing agent with control agent i.e. silicon carbide-carbon and silicon carbide-sugar is very effective in production of expanded micro-inclusions.
- 2- Waste glass is an economical and suitable addition to various silicate mixtures.
- 3- Silicate raw materials, appropriate for production of expanded micro-inclusions according to the method of present invention can be selected from a wide range of waste byproducts, minerals, chemicals, and rocks.

### Example 3

15 This example illustrates a method to make expanded micro-inclusions from formulations consisting of various quantities of volcanic ash, sodium hydroxide, mixtures of blowing and control agents and other minor additives.

#### Formulation 3A

20 A sample was prepared by mixing 78.2 grams of volcanic ash; ground to a d<sub>50</sub> particle size of about 3 microns, with 20 grams of solid sodium hydroxide (flakes), 0.8 grams of a commercial grade silicon carbide as the primary blowing agent, 1 gram of a commercial grade carbon black as the control agent and 43mL of water.



Formulation 3B and 3C

- Samples were prepared using a blend of volcanic ash and iron (III) oxide that was co-ground to a  $d_{50}$  particle size of approximately 1 micron. The formulations are shown in Table 7. The composition of the volcanic ash is given in Table 5. The mixture
- 5 was blended into homogeneous slurry, poured into a flat dish and allowed to solidify at room temperature for approximately 5 minutes. The resulting product was further dried at about 50 degrees Celsius for about 20 hours, after which it was ground and sieved to obtain powders within a size range of 106 to 180 microns. In the next step, the powders were fed into a vertical heated tube furnace at an approximate feed rate of 0.14 g/min.
- 10 The constant temperature zone of the furnace could be adjusted to provide residence times from less than one second to approximately several seconds at the peak firing temperatures. The foamed micro-inclusions were collected on a funnel shaped collecting device covered with a fine mesh screen positioned at the bottom portion of the furnace. A mild suction was applied to the end of funnel to aid in collecting the micro-inclusions.
- 15 The products were characterized for particle density (e.g. apparent density), and microscopic examination by SEM.

The results are summarized in Table 8.

Figures 17 to 20 show two cross sections per sample, of the products of Formulations 3A to 3C respectively.

20

Table 7. Formulations (grams) 3A to 3C

Formulation No.	Volcanic Ash	Sodium Hydroxide	Blowing Agents	Control Agents	Iron (III) Oxide	Water (mL)
3A	78.2	20.0	0.8 SiC	1.0 Carbon Black		43
3B	76.6	19.6	0.8	1.0 Carbon Black	2.0	43
3C	86.2	9.8	0.8	1.0 Carbon Black	2.2	43

Table 8. Result Summary

Formulation No.	Temperature (degree C)	Residence time (second)	Apparent density ( $\text{g/cm}^3$ )
3A	1200	0.6-1.1	0.71
3B	1200	0.6-1.1	0.60
3C	1200	0.6-1.1	0.59

Following conclusions can be drawn from Example 3.

- 1- Combination of silicon carbide as primary blowing agent and carbon black as control agent is very effective in expanding volcanic ash into very light rounded product.
- 5 2- As sodium concentration is increased in the formulation, the product roundness approaches near spherical shape. Sodium oxide is a powerful fluxing agent for silicate glasses, e.g. viscosity reducer. Therefore, less viscous formulations tend to form spherical expanded particles rather than only rounded micro-particles, primarily because of lower surface tension at  
10 the firing temperature.

#### Example 4

This example illustrates a method to make expanded micro-inclusions from formulations consisting of fly ash, sodium hydroxide, and blowing control agents.

##### Formulation 4A

- 15 A sample was prepared by mixing 79 grams of a type F fly ash; ground to a  $d_{50}$  particle size of about 4 microns, with 19 grams of solid sodium hydroxide (flakes), 1 gram of a commercial grade silicon carbide as the primary blowing agent, 1 gram of a commercial grade carbon black as the control agent and 42mL of water.

##### Formulation 4B

- 20 A sample was made by mixing 68.7 grams of a type F fly ash similar to the one used in formulation 4A, with 29.5 grams of solid sodium hydroxide, as shown in Table 9. The composition of the fly ash is given in Table 5.

- The mixture was blended into homogeneous slurry, poured into a flat dish and allowed to solidify at room temperature for approximately 5 minutes. The resulting  
25 product was further dried at about 50 degrees Celsius for about 20 hours, after which it was ground and sieved to obtain powders within a size range of 106 to 180 microns. In the next step, the powders were fed into a vertical heated tube furnace at an approximate feed rate of 0.14 g/min. The constant temperature zone of the furnace could be adjusted to provide residence times from less than one second to approximately several seconds  
30 at the peak firing temperatures. The foamed micro-inclusions were collected on a funnel shaped collecting device covered with a fine mesh screen positioned at the bottom portion of the furnace. A mild suction was applied to the end of funnel to aid in

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collecting the micro-inclusions. The products were characterized for particle density (e.g. apparent density), and microscopic examination by SEM.

The results are summarized in Table 10.

Figures 21 and 22 show two cross sections per sample, of the products of

5 Formulations 4A and 4B respectively.

Table 9. Formulations (grams) 4A and 4B

Formulation No.	Fly ash	Sodium Hydroxide	Blowing Agent	Control Agent	Water (mL)
4A	79.0	19.0	1.0 SiC	1.0 Carbon Black	42.0
4B	68.7	29.5	0.8 SiC	1.0 Carbon Black	43.0

Table 10. Result Summary

Formulation No.	Temperature (degree C)	Residence time (second)	Apparent density (g/cm <sup>3</sup> )
4A	1200	0.6-1.1	0.67
4B	1200	0.6-1.1	1.03

10

Following conclusions can be drawn from Example 4.

- 1- A combination of silicon carbide as the primary blowing agent and carbon as the control agent is very effective in producing low density micro-inclusions from a silicate waste byproduct, fly ash.
- 15 2- The concentration of fluxing compound (e.g. sodium hydroxide?) can be optimized to produce excellent spherical micro-inclusions with low particle density.
- 3- Higher concentration of fluxing agent beyond an optimum value, not only increases the particle density of the product, but also negatively impacts the economy. Waste fly ash is much less expensive than sodium hydroxide.
- 20

#### Example 5

This example illustrates a method to make expanded micro-inclusions from a formulation consisting of phosphatic clay a waste byproduct from phosphate ore beneficiation, sodium hydroxide, silicon carbide and carbon black.

25 Formulation 5A

A sample was prepared by mixing 88.4 grams of phosphatic clay; ground to a d<sub>50</sub> particle size of 0.6 microns, with 9.8 grams of solid sodium hydroxide (flakes), 0.8 grams of a commercial grade silicon carbide, 1.0 grams of a commercial grade carbon

black and 85mL of water. The composition of the phosphatic clay is given in Table 11. The mixture was blended into homogeneous slurry, poured into a flat dish and allowed to solidify at room temperature for approximately 5 minutes. The resulting product was further dried at about 50 degrees Celsius for about 20 hours, after which it was ground and sieved to obtain powders within a size range of 106 to 180 microns. In the next step, the powders were fed into a vertical heated tube furnace at an approximate feed rate of 0.14 g/min. The constant temperature zone of the furnace could be adjusted to provide residence times from less than one second to approximately several seconds at the peak firing temperatures. The foamed micro-inclusions were collected on a funnel shaped collecting device covered with a fine mesh screen positioned at the bottom portion of the furnace. A mild suction was applied to the end of funnel to aid in collecting the micro-inclusions. The products were characterized for particle density (e.g. apparent density), and microscopic examination by SEM.

The results are summarized in Table 12.

Figures 35 and 36 show the cross section of the product.

Table 11. Chemical Composition of Phosphatic Clay

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	Mn <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Total
36.5	17.8	2.7	20.8	3.4	0.33	0.29	0.88	0.57	0.05	16.7	100.0

Table 12. Result Summary

Temperature (degree C)	Residence time (second)	Apparent density (g/cm <sup>3</sup> )
1300	0.8-1.5	0.92

Following conclusions can be drawn from Example 5.

- 1- Multi-blowing agent combination of silicon carbide and carbon has been effectively used to produce low density micro-inclusions from a waste clay byproduct.
- 2- The P<sub>2</sub>O<sub>5</sub>-CaO combined concentration is more than 33% of the total wt% of the product. The combination can potentially form an amorphous apatite phase in the product.

Apatite containing product may exhibit useful bioactive reactions in medical applications.

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It will be understood that the present invention may be embodied in other forms without departing from the spirit or scope of the inventive idea.

**CLAIMS**

1. A method of producing a low density material comprising providing a precursor by forming an aqueous mixture of inorganic primary component and a blowing agent,  
5 drying the mixture and optionally grinding to a predetermined particle size and firing the precursor to activate the blowing agent to expand the precursor and form a low density material wherein  
activation of the blowing agent is controlled such that the blowing agent is activated within a predetermined optimal temperature range.
- 10 2. A method as claimed in claim 1 wherein the low density material is a microparticle with a diameter of up to 1,000 microns.
3. A method as claimed in any one of claims 1-3 wherein the blowing agent is activated within a temperature range in which the inorganic primary component has melted and is within an optimal viscosity range.
- 15 4. A method as claimed in any one of the preceding claims wherein the blowing agent is controlled by addition of a control agent.
5. A method as claimed in any one of the preceding claims wherein the blowing agent is provided as a primary blowing agent, and the control agent is provided as a secondary blowing agent.
- 20 6. A method as claimed in any one of the preceding claims wherein the primary blowing agent has a first activation temperature and the secondary blowing agent has a second activation temperature which is less than the first activation temperature.
7. The method of any one of the preceding claims, wherein the primary blowing agent is selected from powdered coal, carbon black, activated carbon, graphite,  
25 carbonaceous polymeric organics, oils, carbohydrates such as sugar, corn syrup or starch, PVA, carbonates, carbides, sulfates, sulfides, nitrides, nitrates, amines, polyols, glycols or glycerine.
8. The method of any one of the preceding claims, wherein the secondary blowing agent is selected from powdered coal, carbon black, activated carbon, graphite,  
30 carbonaceous polymeric organics, oils, carbohydrates such as sugar, corn syrup or starch, PVA, carbonates, carbides, sulfates, sulfides, nitrides, nitrates, amines, polyols, glycols or glycerine.

9. The method of any one of the preceding claims, wherein the precursor further comprises a tertiary blowing agent having a third activation temperature, wherein the third activation temperature is less than the first activation temperature.
10. The method as claimed in claim 9, wherein the tertiary blowing agent is selected  
5 from powdered coal, carbon black, activated carbon, graphite, carbonaceous polymeric organics, oils, carbohydrates, PVA, carbonates, sulfates, sulfides, nitrates, amines, polyols, glycols or glycerine.
11. A method according to any one of the preceding claims wherein firing of the precursor is conducted under such conditions as to control activation of the blowing  
10 agent.
12. A method according to any one of the preceding claims wherein firing of the precursor is conducted in an oxygen deficient environment.
13. A method as claimed in claim 12 wherein firing of the precursor is conducted in a fuel rich/less oxidising environment.
- 15 14. A method according to any one of the preceding claims wherein activation of the blowing agent is controlled by appropriate dosing with O<sub>2</sub> depleting or O<sub>2</sub> enriching gases during firing of the precursor.
15. A method according to any one of the preceding claims wherein the precursor is formed with a predetermined distribution of blowing agent there through, said  
20 distribution providing a controlled activation of the blowing agent during firing of the precursor.
16. The method of claim 1, wherein the drying step is performed using a spray dryer having an aqueous slurry feed.
17. The method of claim 16, wherein the spray dryer has an inlet temperature in the  
25 range of 300 to 600°C.
18. The method of claims 16 or 17, wherein the spray dryer has an outlet temperature in the range of 90 to 220°C.
19. The method of any one of the preceding claims, wherein the amount of inorganic primary component is at least 50 wt.%, based on the total dry weight of the agglomerate  
30 precursor.
20. The method of any one of the preceding claims, wherein the amount of blowing component is in the range of 0.05 to 10 wt.%, based on the total dry weight of the agglomerate precursor.

21. The method of any one of the preceding claims wherein the ratio of inorganic primary component to blowing component is in the range of 1000:1 to 10:1.
22. The method of any one of the preceding claims, wherein the mixture is dried such that the water content of the precursor is less than about 14 wt.%.
- 5 23. The method of any one of the preceding claims, wherein the resultant agglomerate precursors have an average agglomerate particle size in the range of 10 to 1000 microns.
24. The method of any one of the preceding claims, wherein the resultant agglomerate precursors have a total alkali metal oxide content of about 10 wt.% or less,  
10 based on the total dry weight of the agglomerate precursor.
25. The method of any one of the preceding claims, wherein the inorganic primary component comprises at least one material selected from inorganic oxides, non-oxides, salts or combinations thereof.
26. The method of any one of the preceding claims, wherein the inorganic primary  
15 component comprises at least one material selected from industrial and/or residential by-products, minerals, rocks, clays, technical grade chemicals or combinations thereof.
27. The method of any one of the preceding claims, wherein the inorganic primary component comprises at least one silicate material.
28. The method of claim 27, wherein the at least one silicate material is selected  
20 from fly ash, bottom ash, blast-furnace slag, paper ash, basaltic rock, andesitic rock, feldspars, aluminosilicate clays, bauxite, volcanic ash, volcanic rocks, volcanic glasses, geopolymers, or combinations thereof.
29. The method of any one of the preceding claims, wherein the inorganic primary component is capable of forming a viscoelastic liquid.
- 25 30. The method of any one of the preceding claims, wherein the inorganic primary component has an average primary particle size in the range of 0.01 to 100 microns.
31. The method of any one of the preceding claims, wherein the primary blowing agent is relatively less water-soluble than the secondary blowing agent.
32. The method of any one of the preceding claims, wherein the blowing agent has  
30 an average particle size in the range of 0.01 to 10 microns.
33. The method of any one of the preceding claims, further comprising mixing a binding agent with the inorganic primary component and the blowing agent.



34. The method of claim 33, wherein the binding agent is selected from alkali metal silicates, alkali metal aluminosilicates, alkali metal borates, alkali or alkaline earth metal carbonates, alkali or alkaline earth metal nitrates, alkali or alkaline earth metal nitrites, boric acid, alkali or alkaline earth metal sulfates, alkali or alkaline earth metal phosphates, alkali or alkaline earth metal hydroxides, carbohydrates, colloidal silica, ultrafine fly ash, Type C fly ash, Type F fly ash, inorganic silicate cements, Portland cement, alumina cement, lime-based cement, phosphate-based cement, organic polymers or combinations thereof.
35. The method of claims 33 or 34, wherein the binding agent has a melting point which is lower than the melting point of the resultant agglomerate precursor as a whole.
36. The method of any one of claims 32 to 34, wherein the binding agent has a melting point in the range of 700 to 1000°C.
37. The method of claim 35 or 36, wherein the binding agent is a silicate.
38. The method of claim 35 or 36, wherein the binding agent is an alkali metal silicate generated by *in situ* reaction of an alkali metal hydroxide and an silicate primary component.
39. The method of any one of claims 35 to 38, wherein the amount of binding agent is in the range of 0.1 to 50 wt.%, based on the total dry weight of the agglomerate precursor.
40. The method of any of claims 35 to 39, wherein the binding agent is relatively more water-soluble than the primary blowing agent.
41. The method of any one of the preceding claims, wherein the primary component, the blowing component and, optionally, the binding agent are co-ground together.
42. A method of forming a precursor for a low density material comprising the steps of:
- (g) providing an inorganic primary component;
  - (h) forming an aqueous mixture of the inorganic primary component, a blowing agent and a control agent, and;
  - (i) drying the mixture to provide an expandable precursor for forming a low density material wherein
- said blowing agent and control agent are selected to control activation of the blowing agent such that the blowing agent is activated within a predetermined optimal temperature range.

43. A method as claimed in claim 42, wherein the blowing agent is provided as a primary blowing agent, and the control agent is provided as a secondary blowing agent.

44. A method as claimed in claims 42 or 43, wherein the primary blowing agent has a first activation temperature and the secondary blowing agent has a second activation temperature which is less than the first activation temperature.

45. The method of any one of claims 42 to 43, wherein the primary blowing agent is selected from powdered coal, carbon black, activated carbon, graphite, carbonaceous polymeric organics, oils, carbohydrates such as sugar, corn syrup or starch, PVA, carbonates, carbides, sulfates, sulfides, nitrides, nitrates, amines, polyols, glycols or glycerine.

46. The method of any one of claims 42 to 45, wherein the secondary blowing agent is selected from powdered coal, carbon black, activated carbon, graphite, carbonaceous polymeric organics, oils, carbohydrates such as sugar, corn syrup or starch, PVA, carbonates, carbides, sulfates, sulfides, nitrides, nitrates, amines, polyols, glycols or glycerine.

47. The method of any one of claims 42 to 46, wherein the precursor further comprises a tertiary blowing agent having a third activation temperature, wherein the third activation temperature is less than the first activation temperature.

48. The method as claimed in claim 47, wherein the tertiary blowing agent is selected from powdered coal, carbon black, activated carbon, graphite, carbonaceous polymeric organics, oils, carbohydrates, PVA, carbonates, sulfates, sulfides, nitrates, amines, polyols, glycols or glycerine.

49. A method according to any one of claims 42 to 48 wherein activation of the blowing agent is controlled by appropriate dosing with O<sub>2</sub> depleting or O<sub>2</sub> enriching gases during firing of the precursor.

50. A method according to any one of claims 42 to 49 wherein the precursor is formed with a predetermined distribution of blowing agent there through, said distribution providing a controlled activation of the blowing agent during firing of the precursor.

51. The method of claim 42, wherein the drying step is performed using a spray dryer having an aqueous slurry feed.

52. The method of claim 51, wherein the spray dryer has an inlet temperature in the range of 300 to 600°C.

53. The method of claims 51 or 52, wherein the spray dryer has an outlet temperature in the range of 90 to 220°C.
54. The method of any one of claims 42 to 53, wherein the amount of inorganic primary component is at least 50 wt.%, based on the total dry weight of the agglomerate precursor.
55. The method of any one of claims 42 to 54, wherein the amount of blowing component is in the range of 0.05 to 10 wt.%, based on the total dry weight of the agglomerate precursor.
56. The method of any one of claims 42 to 55 wherein the ratio of inorganic primary component to blowing component is in the range of 1000:1 to 10:1.
57. The method of any one of claims 42 to 56, wherein the mixture is dried such that the water content of the precursor is less than about 14 wt.%.
58. The method of any one of claims 42 to 57, wherein the resultant agglomerate precursors have an average agglomerate particle size in the range of 10 to 1000 microns.
59. The method of any one of claims 42 to 58, wherein the resultant agglomerate precursors have a total alkali metal oxide content of about 10 wt.% or less, based on the total dry weight of the agglomerate precursor.
60. The method of any one of claims 42 to 59, wherein the inorganic primary component comprises at least one material selected from inorganic oxides, non-oxides, salts or combinations thereof.
61. The method of any one of claims 42 to 60, wherein the inorganic primary component comprises at least one material selected from industrial and/or residential by-products, minerals, rocks, clays, technical grade chemicals or combinations thereof.
62. The method of any one of claims 42 to 61, wherein the inorganic primary component comprises at least one silicate material.
63. The method of claim 62, wherein the at least one silicate material is selected from fly ash, bottom ash, blast-furnace slag, paper ash, basaltic rock, andesitic rock, feldspars, aluminosilicate clays, bauxite, volcanic ash, volcanic rocks, volcanic glasses, geopolymers, or combinations thereof.
64. The method of any one of claims 42 to 63, wherein the inorganic primary component is capable of forming a viscoelastic liquid.

65. The method of any one of claims 42 to 64, wherein the inorganic primary component has an average primary particle size in the range of 0.01 to 100 microns.
66. The method of any one of claims 42 to 65, wherein the primary blowing agent is relatively less water-soluble than the secondary blowing agent.
- 5 67. The method of any one of claims 42 to 66, wherein the blowing agent has an average particle size in the range of 0.01 to 10 microns.
68. The method of any one of 42 to 67 claims, further comprising mixing a binding agent with the inorganic primary component and the blowing agent.
69. The method of claim 68, wherein the binding agent is selected from alkali metal  
10 silicates, alkali metal aluminosilicates, alkali metal borates, alkali or alkaline earth metal carbonates, alkali or alkaline earth metal nitrates, alkali or alkaline earth metal nitrites, boric acid, alkali or alkaline earth metal sulfates, alkali or alkaline earth metal phosphates, alkali or alkaline earth metal hydroxides, carbohydrates, colloidal silica, ultrafine fly ash, Type C fly ash, Type F fly ash, inorganic silicate cements, Portland  
15 cement, alumina cement, lime-based cement, phosphate-based cement, organic polymers or combinations thereof.
70. The method of claims 68 or 69, wherein the binding agent has a melting point which is lower than the melting point of the resultant agglomerate precursor as a whole.
71. The method of any one of claims 68 to 70, wherein the binding agent has a  
20 melting point in the range of 700 to 1000°C.
72. The method of claim 70 or 71, wherein the binding agent is a silicate.
73. The method of any one of claims 70 or 71, wherein the binding agent is an alkali metal silicate generated by *in situ* reaction of an alkali metal hydroxide and an silicate primary component.
- 25 74. The method of any one of claims 70 to 73, wherein the amount of binding agent is in the range of 0.1 to 50 wt.%, based on the total dry weight of the agglomerate precursor.
75. The method of any of claims 70 to 74, wherein the binding agent is relatively more water-soluble than the primary blowing agent.
- 30 76. The method of any one of claims 42 to 75, wherein the primary component, the blowing component and, optionally, the binding agent are co-ground together.

77. A method of forming a precursor for a low density material comprising the steps of:

- (j) providing an inorganic primary component;
- (k) forming an aqueous mixture of the inorganic primary component and a blowing agent; and
- (l) drying the mixture to provide an expandable precursor for forming a low density material wherein said blowing agent is selected and/or distributed in the precursor to control activation of the blowing agent upon firing of the precursor such that the blowing agent is activated within a predetermined optimal temperature range.

78. A precursor suitable for producing expanded micro particles, said precursor comprising an expandable inorganic primary component, a blowing agent adapted to be activated and thereby expand said primary component, and a control agent selected to control activation of the blowing agent such that the blowing agent is activated within a predetermined optimal temperature range.

79. A precursor according to claim 78 wherein the blowing agent is provided as a primary blowing agent, and the control agent is provided as a secondary blowing agent.

80. A precursor as claimed in claim 78 or 79 wherein the primary blowing agent has a first activation temperature and the secondary blowing agent has a second activation temperature which is less than the first activation temperature.

81. A precursor as claimed in any one of claims 78 to 80, wherein the primary blowing agent is selected from powdered coal, carbon black, activated carbon, graphite, carbonaceous polymeric organics, oils, carbohydrates such as sugar, corn syrup or starch, PVA, carbonates, carbides, sulfates, sulfides, nitrides, nitrates, amines, polyols, glycols or glycerine.

82. A precursor as claimed in any one of claims 78 to 81, wherein the secondary blowing agent is selected from powdered coal, carbon black, activated carbon, graphite, carbonaceous polymeric organics, oils, carbohydrates such as sugar, corn syrup or starch, PVA, carbonates, carbides, sulfates, sulfides, nitrides, nitrates, amines, polyols, glycols or glycerine.

83. A precursor as claimed in any one of claims 78 to 82, wherein the precursor further comprises a tertiary blowing agent having a third activation temperature, wherein the third activation temperature is less than the first activation temperature.
84. A precursor as claimed in claim 83, wherein the tertiary blowing agent is selected  
5 from powdered coal, carbon black, activated carbon, graphite, carbonaceous polymeric organics, oils, carbohydrates, PVA, carbonates, sulfates, sulfides, nitrates, amines, polyols, glycols or glycerine.
85. A precursor as claimed in any one of claims 78 to 84 wherein activation of the blowing agent is controlled by appropriate dosing with O<sub>2</sub> depleting or O<sub>2</sub> enriching  
10 gases during firing of the precursor.
86. A precursor as claimed in any one of claims 78 to 85 wherein the precursor is formed with a predetermined distribution of blowing agent there through, said distribution providing a controlled activation of the blowing agent during firing of the precursor.
- 15 87. A precursor as claimed in any one of claims 78 to 86, wherein the amount of inorganic primary component is at least 50 wt.%, based on the total dry weight of the agglomerate precursor.
88. A precursor as claimed in any one of claims 78 to 87, wherein the amount of blowing component is in the range of 0.05 to 10 wt.%, based on the total dry weight of  
20 the agglomerate precursor.
89. A precursor as claimed in any one of claims 78 to 88, wherein the ratio of inorganic primary component to blowing component is in the range of 1000:1 to 10:1.
90. A precursor as claimed in any one of claims 78 to 89, wherein the mixture is dried such that the water content of the precursor is less than about 14 wt.%.
- 25 91. A precursor as claimed in any one of claims 78 to 90, wherein the resultant agglomerate precursors have an average agglomerate particle size in the range of 10 to 1000 microns.
92. A precursor as claimed in any one of claims 78 to 91, wherein the resultant agglomerate precursors have a total alkali metal oxide content of about 10 wt.% or less,  
30 based on the total dry weight of the agglomerate precursor.

93. A precursor as claimed in any one of claims 78 to 92, wherein the inorganic primary component comprises at least one material selected from inorganic oxides, non-oxides, salts or combinations thereof.
94. A precursor as claimed in any one of claims 78 to 93, wherein the inorganic  
5 primary component comprises at least one material selected from industrial and/or residential by-products, minerals, rocks, clays, technical grade chemicals or combinations thereof.
95. A precursor as claimed in any one of claims 79 to 94, wherein the inorganic primary component comprises at least one silicate material.
- 10 96. A precursor as claimed in claim 95, wherein the at least one silicate material is selected from fly ash, bottom ash, blast-furnace slag, paper ash, basaltic rock, andesitic rock, feldspars, aluminosilicate clays, bauxite, volcanic ash, volcanic rocks, volcanic glasses, geopolymers, or combinations thereof.
97. A precursor as claimed in any one of claims 78 to 96, wherein the inorganic  
15 primary component is capable of forming a viscoelastic liquid.
98. A precursor as claimed in any one of claims 78 to 97, wherein the inorganic primary component has an average primary particle size in the range of 0.01 to 100 microns.
99. A precursor as claimed in any one 78 to 98, of the preceding claims, wherein the  
20 primary blowing agent is relatively less water-soluble than the secondary blowing agent.
100. A precursor as claimed in any one of claims 78 to 99, wherein the blowing agent has an average particle size in the range of 0.01 to 10 microns.
101. A precursor as claimed in any one of claims 78 to 100, further comprising mixing a binding agent with the inorganic primary component and the blowing agent.
- 25 102. A precursor as claimed in claim 101, wherein the binding agent is selected from alkali metal silicates, alkali metal aluminosilicates, alkali metal borates, alkali or alkaline earth metal carbonates, alkali or alkaline earth metal nitrates, alkali or alkaline earth metal nitrites, boric acid, alkali or alkaline earth metal sulfates, alkali or alkaline earth metal phosphates, alkali or alkaline earth metal hydroxides, carbohydrates, colloidal  
30 silica, ultrafine fly ash, Type C fly ash, Type F fly ash, inorganic silicate cements, Portland cement, alumina cement, lime-based cement, phosphate-based cement, organic polymers or combinations thereof.

103. A precursor as claimed in claim 101 or 102, wherein the binding agent has a melting point which is lower than the melting point of the resultant agglomerate precursor as a whole.
104. A precursor as claimed in any one of claims 101 to 103, wherein the binding agent has a melting point in the range of 700 to 1000°C.
105. A precursor as claimed in claim 103 or 104, wherein the binding agent is a silicate.
106. A precursor as claimed in claim 103 or 104, wherein the binding agent is an alkali metal silicate generated by *in situ* reaction of an alkali metal hydroxide and an silicate primary component.
107. A precursor as claimed in any one of claims 103 to 106, wherein the amount of binding agent is in the range of 0.1 to 50 wt.%, based on the total dry weight of the agglomerate precursor.
108. A precursor as claimed in any of claims 103 to 107, wherein the binding agent is relatively more water-soluble than the primary blowing agent.
109. A precursor suitable for producing expanded micro particles, said precursor comprising an expandable inorganic primary component and a blowing agent selected and/or distributed within the precursor to control activation of the blowing agent whereby upon firing of the precursor to produce the expanded micro particles, the blowing agent is activated within a predetermined optimal temperature range.
110. A method of controlling activation of the blowing agent in an inorganic mixture to produce expanded micro particles, said method comprising:  
providing at least one blowing agent which is activated under predetermined conditions to release a blowing gas and produce expanded micro particles and controlling such conditions whereby said activation takes place within a predetermined optimal viscosity range of the inorganic mixture.
111. A blowing component for producing expanded micro particles, said blowing component comprising a primary blowing agent and a predetermined quantity of compatible control agent wherein upon inclusion of such a blowing component within

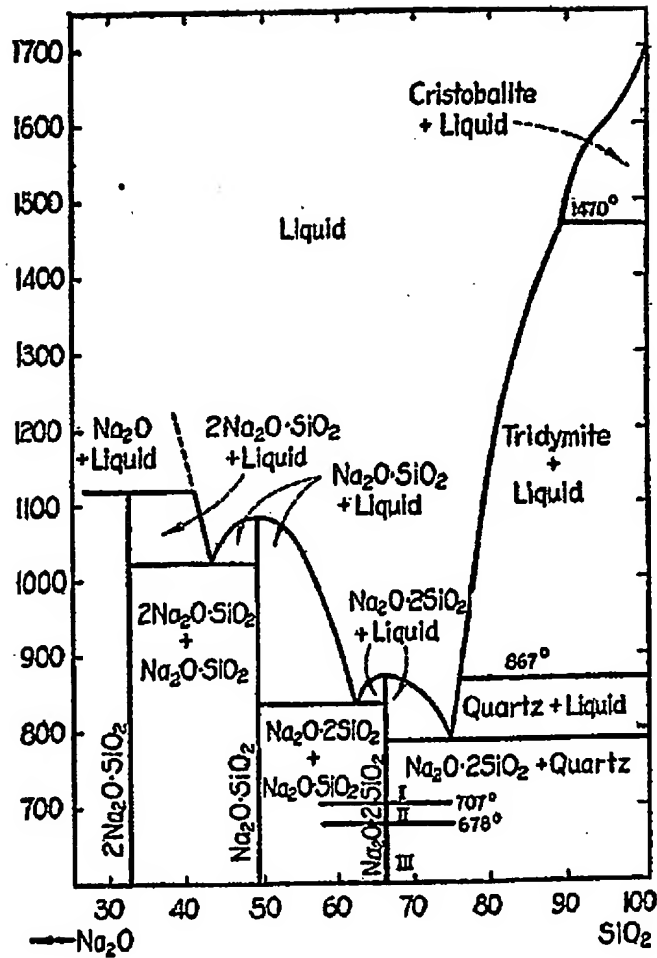


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an expandable mixture, the control agent may be activated prior or simultaneously with the blowing agent to control and conserve the blowing agent.

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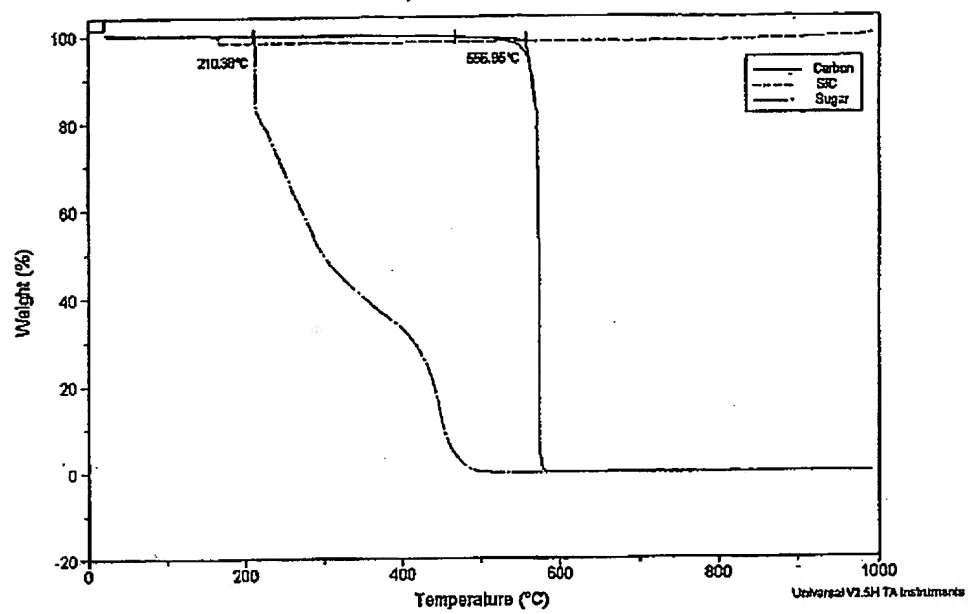
Figure 1

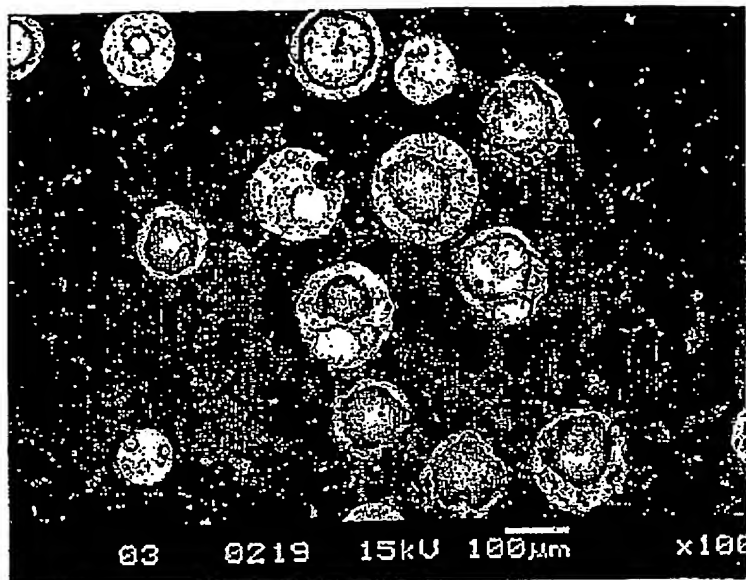
 $\text{Na}_2\text{O}-\text{SiO}_2$ FIG. 192.—System  $\text{SiO}_2-2\text{Na}_2\text{O}\cdot\text{SiO}_2$ .

F. C. Kracek, *J. Phys. Chem.*, 34, 1588 (1930); *J. Am. Chem. Soc.*, 61, 2869 (1939).

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Figure 2





5 Figure 3 (product of Formulation 1A).

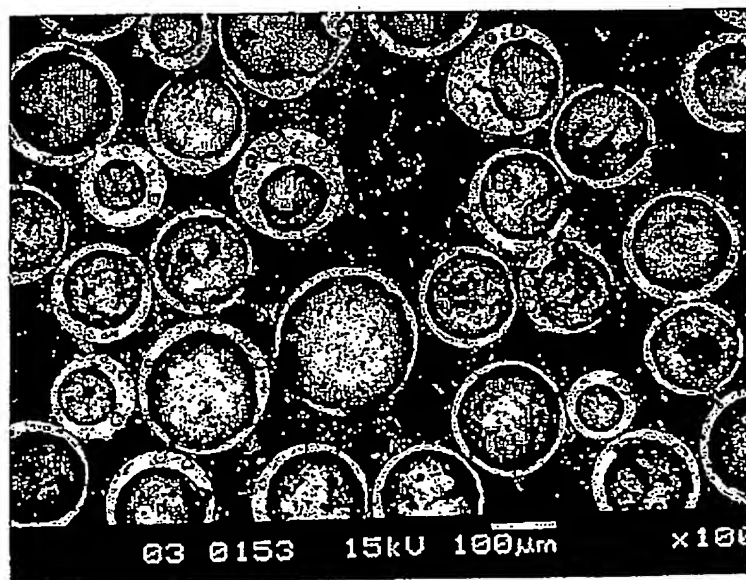


Figure 4 (product of Formulation 1B).

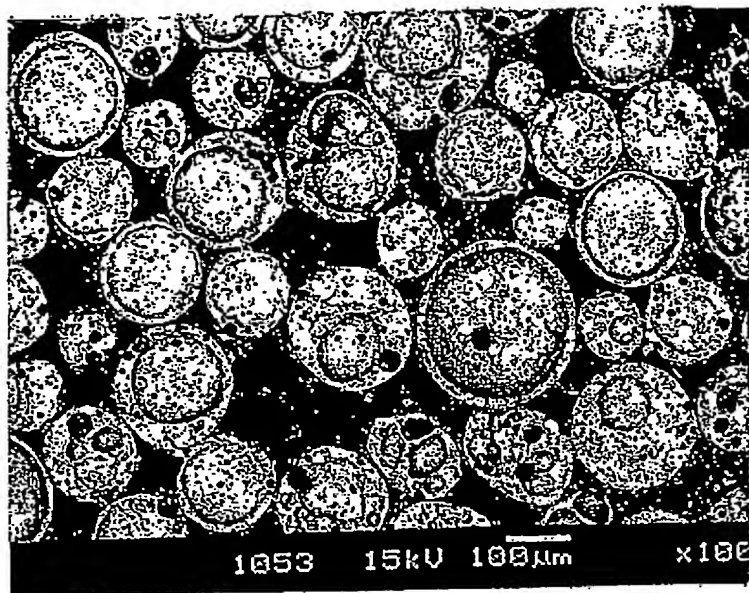
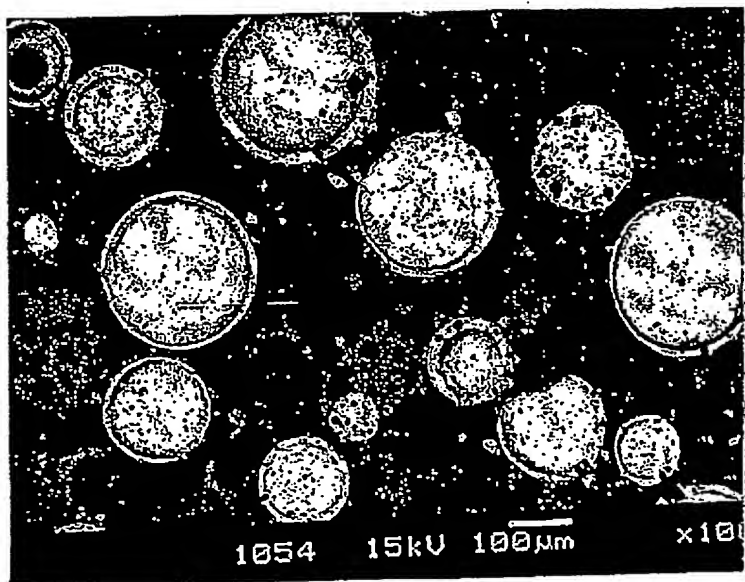


Figure 5 (product of Formulation 1C).



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Figure 6 (product of Formulation 1D).

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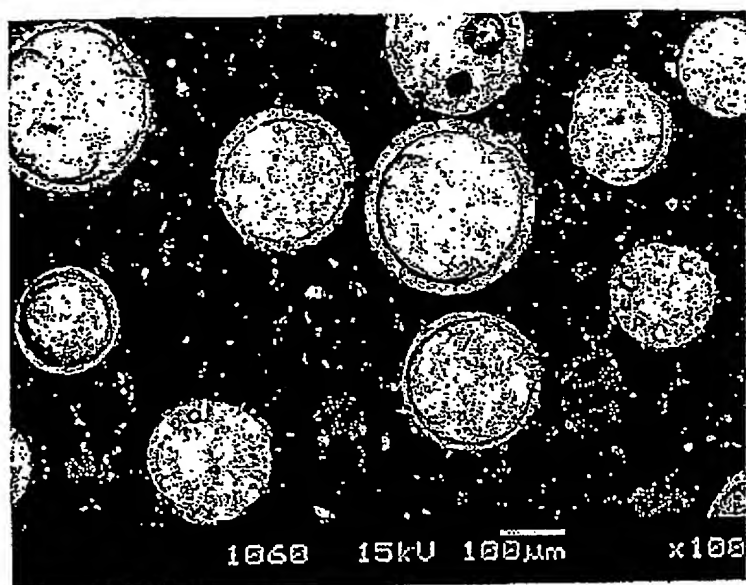
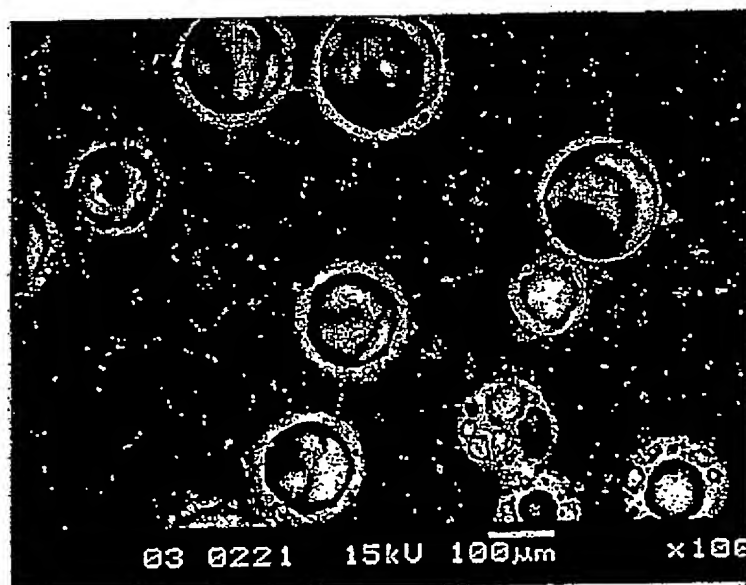


Figure 7 (product of Formulation 1B).



5 Figure 8 (product of Formulation 1F).

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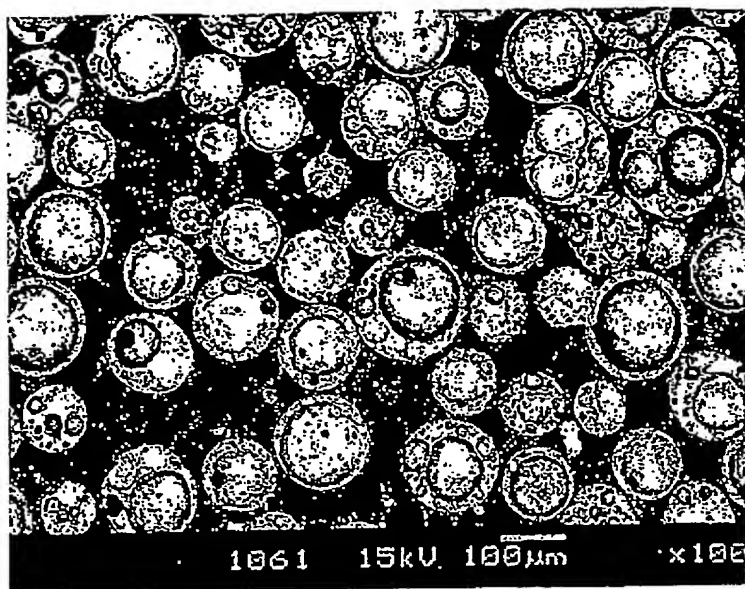
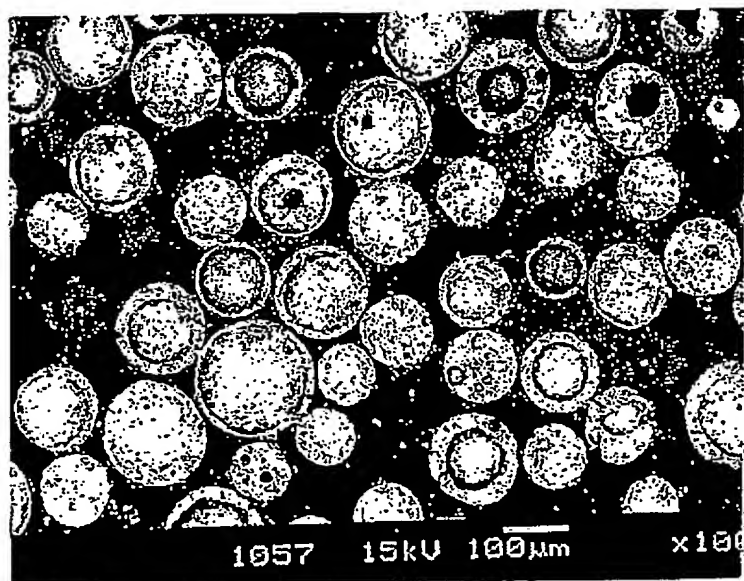


Figure 9 (product of Formulation 2A).



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Figure 10 (product of Formulation 2B).

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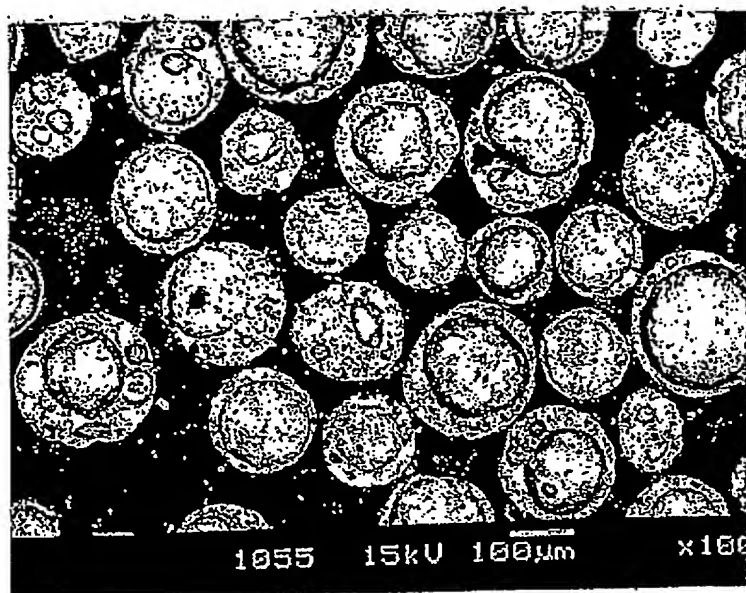


Figure 11 (product of Formulation 2C).

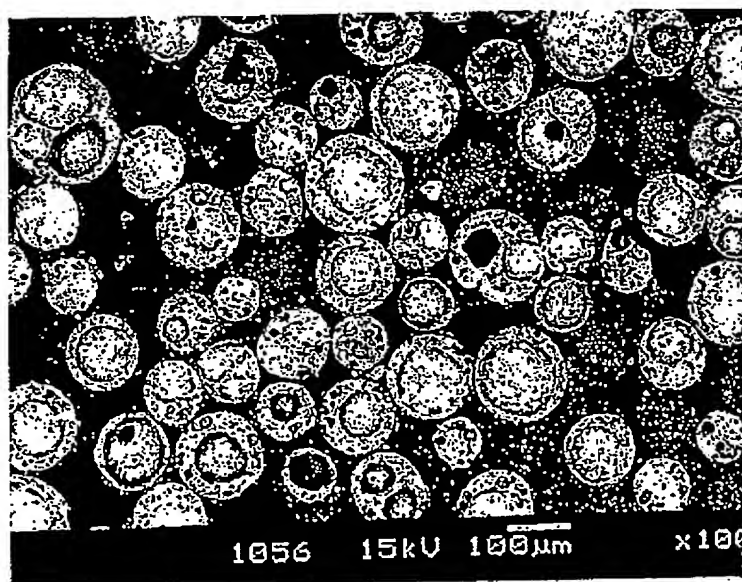


Figure 12 (product of Formulation 2D).



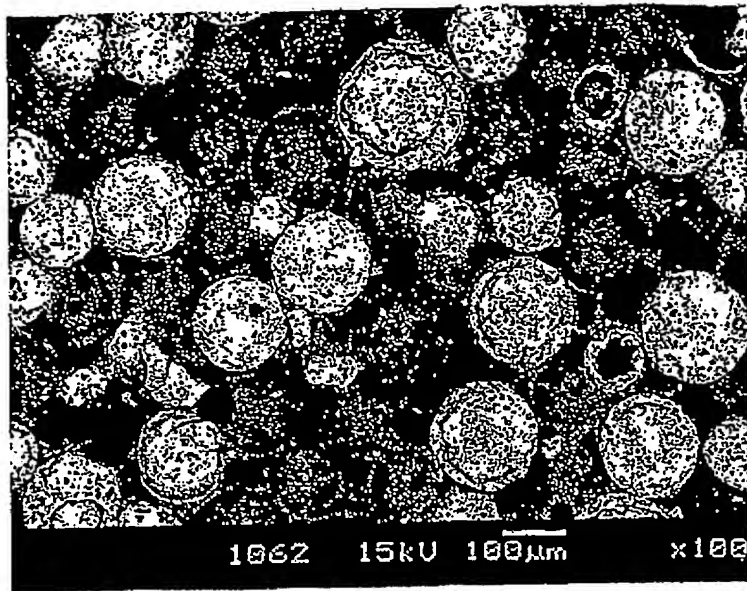
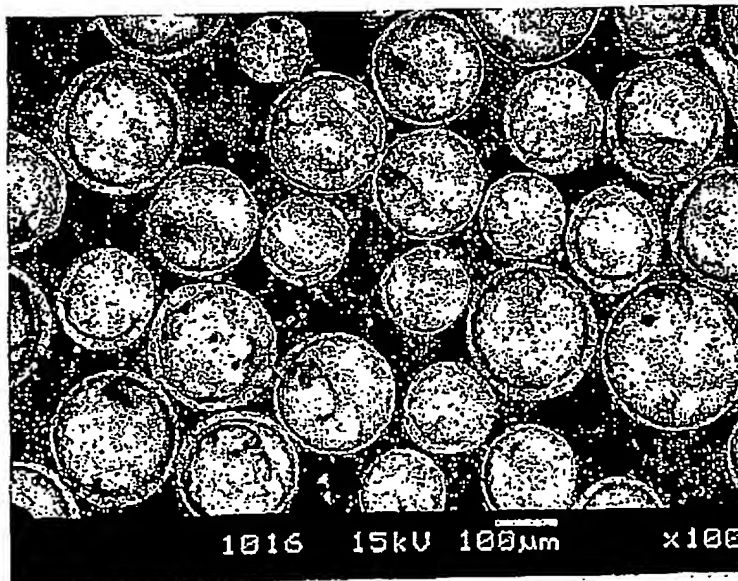


Figure 13 (product of Formulation 2B).



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Figure 14 (product of Formulation 2F).

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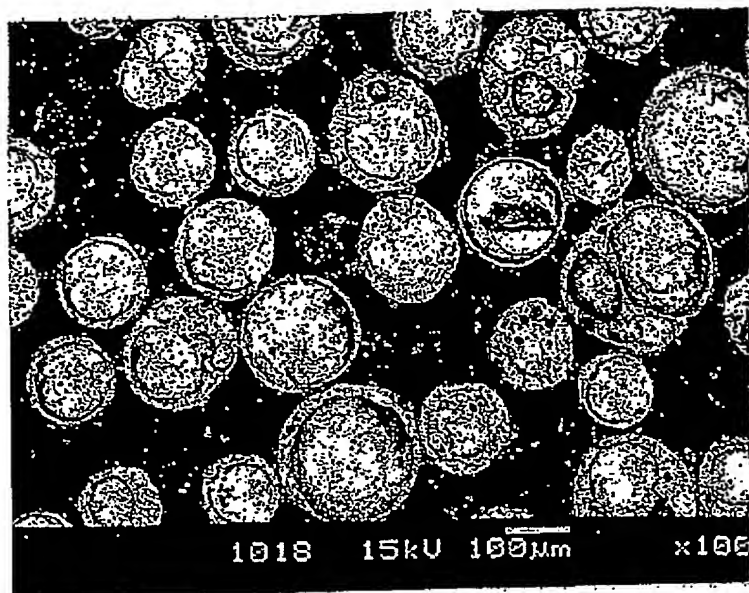
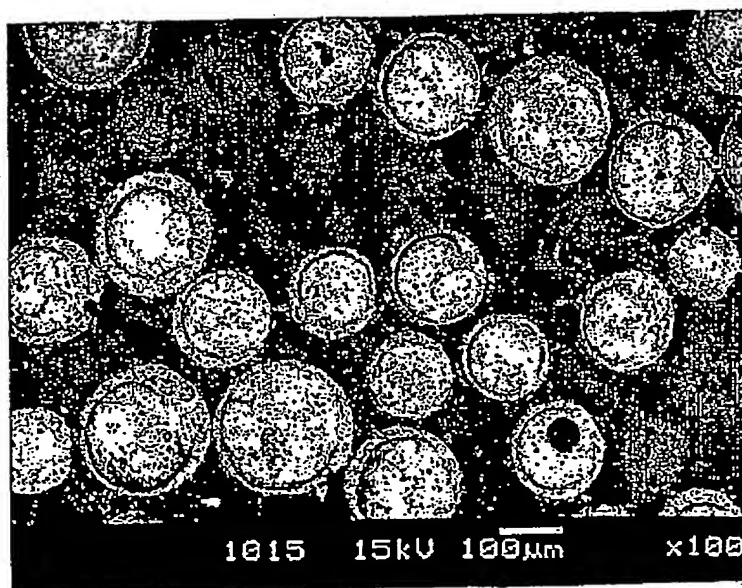


Figure 15 (product of Formulation 3A).



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Figure 16 (product of Formulation 3B).

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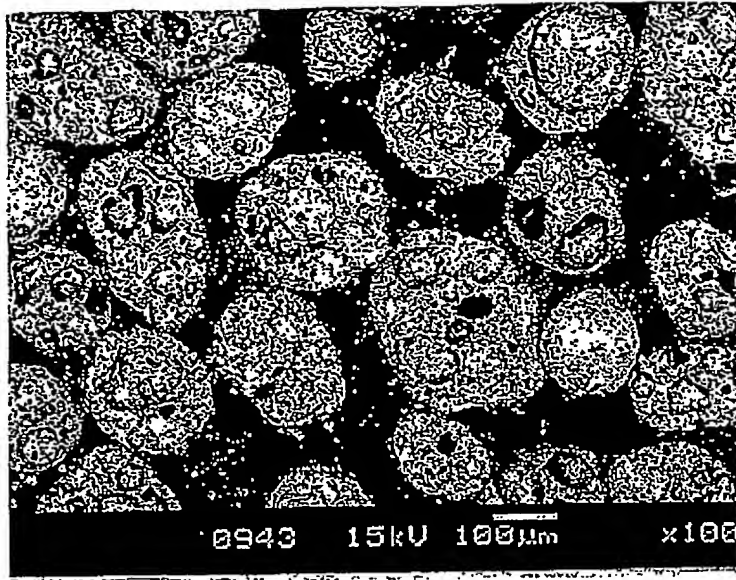


Figure 17 (product of Formulation 3C).

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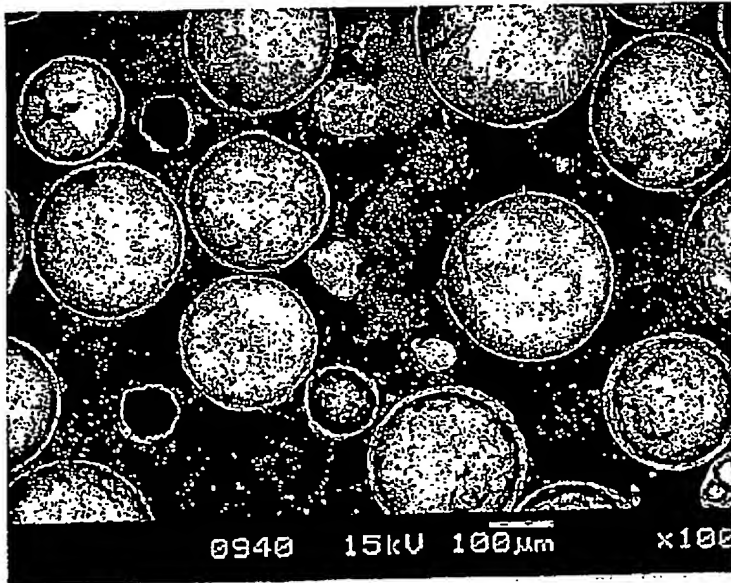


Figure 18 (product of Formulation 4A).

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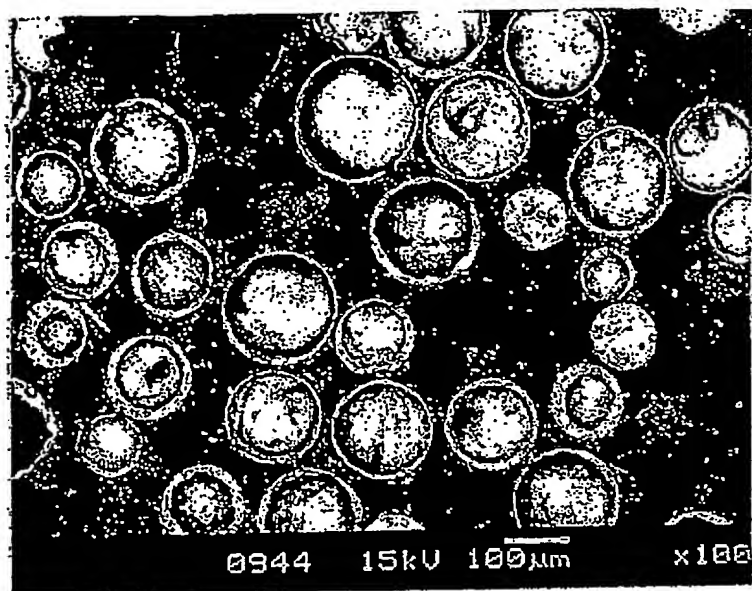
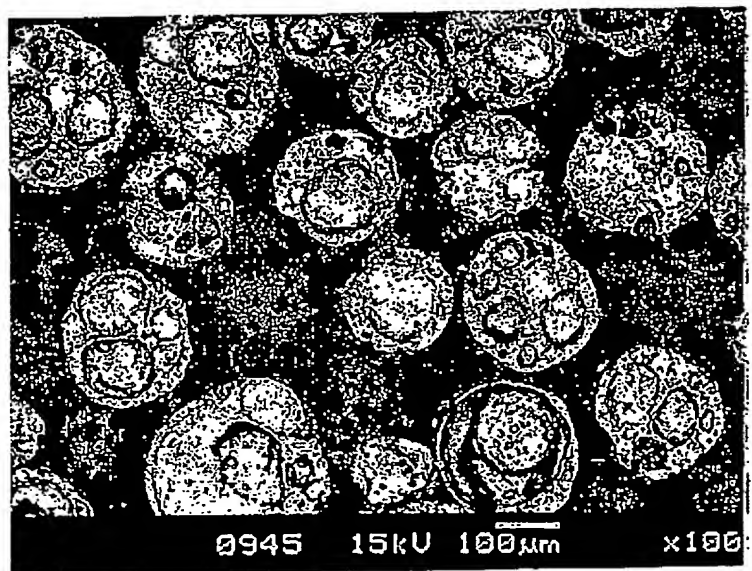


Figure 19 (product of Formulation 4B).



5.

Figure 20 (product of Formulation 5A).

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/AU2004/000241

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. 7: B01J 13/04, C04B 38/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC AS ABOVE

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

File WPAT, JAPIO (IPC and/or keywords)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E,X	WO 2004/018090 A (JAMES HARDIE RESEARCH) 4 March 2004. See whole document.	1-111
X	US 3909283 A (WARNKE) 30 September 1975. See abstract, claims.	1-111
X	US 4336338 A (DOWNS) 22 June 1982. See claims.	1-111
X	US 4340407 A (ANDERSON) 20 July 1982. See claims	1-111

☒ Further documents are listed in the continuation of Box C

☒ See patent family annex

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Date of the actual completion of the international search  
13 April 2004

Date of mailing of the international search report 20 APR 2004

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/AU2004/000241

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 1996/007538 A (THERMACELL TECHNOLOGIES) 24 March 1996. See claims.	1-111
X	WO 2001/072863 A (APACHE PRODUCTS) 26 March 2001. See Claims.	1-111
X	US 5176732 A (BLOCK) 5 January 1993 See abstract, claims.	1-111
X	EP 359362 B1 (ECC INTERNATIONAL) 5 April 1995. See page 3, claims 1, 7, 8 & 11	1-111
X	EP 1160212 A (ASAHI GLASS) 5 December 2001. See claims.	1-111
X	EP 1156021 A (ASAHI GLASS) 21 November 2001. See claims.	1-111
X	EP 801037 B1 (ASAHI GLASS) 16 August 2000. See page 4 and the claims.	1-111
X	US 5458973 A (JEFFS) 17 October 1995. See example and claims.	1-111
X	US 4826788 A (DENNERT) 2 May 1989. See claim 4 and table 1.	1-111

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2004/000241

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member			
WO	2004018090				
US	3909283				
US	4336338				
US	4340407	CA	1168818	DE	3201992
		GB	2092566	JP	57140322
WO	9607538	AU	35478/95	EP	0781196
WO	0172863	AU	49453/01	CA	2403867
				EP	1268593
US	5176732	AU	89666/91	CA	2051837
		HK	43796	JP	4275927
		US	5069702	EP	0493734
EP	0359362	AU	37917/89	BR	8604149
		EP	0213931	ES	2001407
		GB	2220666	JP	2067341
		JP	62096540	NZ	229907
		US	5028482	US	5049594
EP	1160212	JP	2002087831	JP	2002087832
EP	1156021	JP	2002037645	US	2001043996
EP	0801037	JP	9278463	US	5849055
US	548973				
US	4826788	CA	1239151	DE	3428165
				EP	0170978
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